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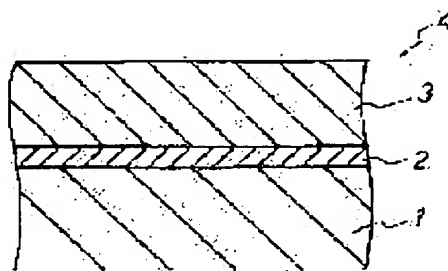
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(54) HEAT RESISTANT MEMBER AND IS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To satisfactorily suppress the transfer of elements between a substrate and a metallic coating layer over a long time, to improve the adhesion of layers and to suppress peeling at the interface.

SOLUTION: An M-Cr-Al-Y alloy layer 3 (M is Ni, Co or Fe) is formed by coating on the surface of a substrate 1 made of an ally based on at least one selected from among Ni, Co and Fe with a diffusion barrier layer 2 in-between to obtain the objective heat resistant member. The diffusion barrier layer has a composition containing at least one kind of metal selected from among Ti, Zr, Hf, V, Ta and Nb as a base and has a metallic layer contg. at least one of O and N allowed to enter into a solid soln. or it is made of a material contg. an $\text{Ma}(\text{A}1-\text{xBx})1-\text{a}$ phase (M is Ni, Co or Fe, A is Al, Ti, Nb or Ta, B is Cr, Mo, W, Hf, Re or Y, $0.3 \leq a \leq 0.8$ and $0 \leq x < 0.5$) deposited in a matrix phase based on at least one kind of element selected from among Ni, Co and Fe.



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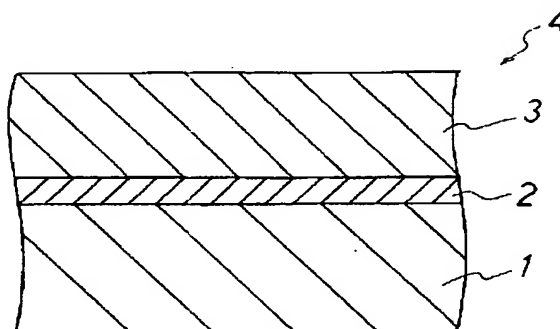
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(54) 【発明の名称】 耐熱部材およびその製造方法

(57) 【要約】

【課題】 長時間にわたって基材/金属コーティング層間の元素移動を十分に抑制することを可能にした上で、各層間の密着性を高めて界面剥離を抑制する。

【解決手段】 Ni、CoおよびFeから選ばれる少なくとも1種を主成分とする合金からなる基材1の表面に、拡散バリア層を介して M-Cr-Al-Y合金層(M=Ni, Co, Fe)を被覆形成した耐熱部材である。拡散バリア層は、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属を主成分とし、酸素および窒素から選ばれる少なくとも1種が固溶した金属層を有する。あるいは、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とするマトリックス相中に、 $M_a(A_{1-x}B_x)_{1-x}$ 相(M=Ni, Co, Fe, A=Al, Ti, Nb, Ta, B=Cr, Mo, W, Hf, Re, Y, $0.3 \leq a \leq 0.8$, $0 \leq x < 0.5$)が析出した材料からなる。



【特許請求の範囲】

【請求項1】 Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材と、前記基材表面に拡散バリア層を介して被覆形成された M-Cr-Al-Y合金層（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を示す）とを具備する耐熱部材において、

前記拡散バリア層は、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属を主成分とし、酸素および窒素から選ばれる少なくとも1種が固溶した金属層を有することを特徴とする耐熱部材。

【請求項2】 Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材と、前記基材表面に拡散バリア層を介して被覆形成された M-Cr-Al-Y合金層（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を示す）とを具備する耐熱部材において、

前記拡散バリア層は、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素とNi、CoおよびFeから選ばれる少なくとも1種の元素との合金を主成分とし、酸素および窒素から選ばれる少なくとも1種が固溶した金属層を有することを特徴とする耐熱部材。

【請求項3】 Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材と、前記基材表面に拡散バリア層を介して被覆形成された M-Cr-Al-Y合金層（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を示す）とを具備する耐熱部材において、

前記拡散バリア層は、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とするマトリックス相中に、 $M_x(A_{1-x}B_x)_{1-x}$ 相（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を、AはAl、Ti、NbおよびTaから選ばれる少なくとも1種の元素を、BはCr、Mo、W、Hf、ReおよびYから選ばれる少なくとも1種の元素を示し、 a および x は $0.3 \leq a \leq 0.8$ 、 $0 \leq x < 0.5$ である）が析出した材料からなり、かつ前記 $M_x(A_{1-x}B_x)_{1-x}$ 相の析出量（体積率）が前記基材中の析出相の体積率より多いことを特徴とする耐熱部材。

【請求項4】 請求項1、請求項2または請求項3記載の耐熱部材において、さらに、前記 M-Cr-Al-Y合金層表面に被覆形成されたセラミックス層を有することを特徴とする耐熱部材。

【請求項5】 Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材表面に、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素を含有する金属層を、酸素分圧または窒素分圧が $0.1 \sim 1 \times 10^4$ Paの雰囲気中で成膜する工程と、前記金属層上に、M-Cr-Al-Y合金層（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を示す）を、 1×10^4 Pa以下の減圧雰囲気中で成膜する工程とを

有することを特徴とする耐熱部材の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、例えばガスタービンの動・静翼の構成材料のように、高温環境下で長時間の高温強度、耐酸化性、耐食性が要求される材料に好適な耐熱部材およびその製造方法に関する。

【0002】

【従来の技術】発電用やエンジン用のガスタービンに代表される高温機器の高効率化を目指した機器使用温度の高温化に伴って、機器構成部品に使用される材料には、一層高レベルの特性、例えば高温強度、高温耐食・耐酸化性等が要求されている。このため、高強度のNi基やCo基の超合金基材の表面に、M-Cr-Al-Y(M=Ni, Co, Fe等)合金等からなる耐食・耐酸化金属コーティングを施す技術が開発され、ガスタービンの動・静翼等においては必須の技術として既に広く適用されている。また、さらなる高温化の流れの中で、耐食・耐酸化金属コーティング層の表面に熱伝導率の低いセラミックス層をコーティングし、内側の金属材料を保護する遮熱コーティング技術も実用化されつつある。

【0003】ところで、従来の金属コーティングの材料開発は、本来の目的である耐食性と耐酸化性の観点から主として行われてきたため、Ni基やCo基の合金基材とM-Cr-Al-Y合金からなる金属コーティング層との材料組成は著しく異なり、その結果として長時間のガスタービン等の運転下において、直接接する基材/金属コーティング層界面で元素移動が生じてしまう。この元素移動によって、金属コーティング層からAlやCr等の保護性酸化物層形成元素が枯渇し、金属コーティング層の耐食・耐酸化性が低下したり、あるいは基材内部での異種相の生成により高温強度が低下する等の問題を招いている。

【0004】上述したような基材/金属コーティング層界面での元素移動に伴う問題を解決するために、基材と金属コーティング層との間に元素拡散を抑制する拡散バリア層を形成することが検討されている。従来、このような拡散バリア層として、内部での元素の拡散係数の小さいAlやTiを主成分とする酸化物層、窒化物層、酸窒化物層等をCVD法等の成膜方法を用いて形成することが試みられているが、拡散バリア層と基材との界面や拡散バリア層と金属コーティング層との界面における密着性が悪く、これら界面で剥離が起きやすいという問題が生じている。この界面での剥離は耐熱部材の寿命低下要因となっている。

【0005】

【発明が解決しようとする課題】上述したように、金属コーティングを適用した耐熱部材、またさらに遮熱コーティングを施した耐熱部材においては、基材/金属コーティング層界面での元素移動に伴う問題を解決するために、拡散バリア層を形成することが試みられているが、

従来の酸化物、窒化物、酸窒化物等を直接被覆形成した拡散バリア層は基材や金属コーティング層との密着性が悪く、これらの界面から剥離が生じて部材寿命を低下させるという問題を有していた。

【0006】このようなことから、従来の耐熱被覆部材においては、基材/金属コーティング層界面での元素移動に伴う劣化を十分に抑制することを可能にすると共に、拡散バリア層自体の密着性を高めることが課題とされていた。

【0007】本発明は、このような課題に対処するためになされたもので、長時間にわたって基材/金属コーティング層間の元素移動を十分に抑制することを可能にすると共に、各層間の密着性を高めて界面剥離を抑制し、長寿命化を達成した耐熱部材を提供することを目的としている。

【0008】

【課題を解決するための手段】本発明における第1の耐熱部材は、請求項1に記載したように、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材と、前記基材表面に拡散バリア層を介して被覆形成されたM-Cr-Al-Y合金層（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を示す。以下同じ）とを具備する耐熱部材において、前記拡散バリア層はTi、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属を主成分とし、酸素および窒素から選ばれる少なくとも1種が固溶した金属層を有すること、あるいは請求項2に記載したように、前記拡散バリア層はTi、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素とNi、CoおよびFeから選ばれる少なくとも1種の元素との合金を主成分とし、酸素および窒素から選ばれる少なくとも1種が固溶した金属層を有することを特徴としている。

【0009】本発明における第2の耐熱部材は、請求項3に記載したように、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材と、前記基材表面に拡散バリア層を介して被覆形成されたM-Cr-Al-Y合金層とを具備する耐熱部材において、前記拡散バリア層は、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とするマトリックス相中に、 $M_1(A_{1-x}B_x)$ 相（ただし、MはNi、CoおよびFeから選ばれる少なくとも1種の元素を、AはAl、Ti、NbおよびTaから選ばれる少なくとも1種の元素を、BはCr、Mo、W、Hf、ReおよびYから選ばれる少なくとも1種の元素を示し、 a および x は $0.3 \leq a \leq 0.8$ 、 $0 \leq x < 0.5$ である）が析出した材料からなり、かつ前記 $M_1(A_{1-x}B_x)$ 相の析出量（体積率）が前記基材中の析出相の体積率より多いことを特徴としている。

【0010】本発明の耐熱部材は、請求項4に記載したように、さらに前記M-Cr-Al-Y合金層表面に被覆形成されたセラミックス層を有していてもよい。

【0011】また、本発明の耐熱部材の製造方法は、請求項5に記載したように、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする合金からなる基材表面に、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素を含有する金属層を、酸素分圧または窒素分圧が $0.1 \sim 1 \times 10^4$ Paの雰囲気中で成膜する工程と、前記金属層上にM-Cr-Al-Y合金層を 1×10^4 Pa以下の減圧雰囲気中で成膜する工程とを有することを特徴としている。

【0012】本発明の第1の耐熱部材においては、拡散バリア層がTi、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属、あるいはこれらとNi、CoおよびFeから選ばれる少なくとも1種の元素との合金を主成分とする金属層を有している。Ti、Zr、Hf、V、Ta、Nb等の金属や、これらとNi、Co、Fe等との合金は、酸素や窒素を多く固溶することができ、この酸素や窒素を多く固溶する金属層はその内部でのAl等の元素の拡散係数が小さいことから、基材とM-Cr-Al-Y合金層との拡散バリア層として機能する。また、上記金属層に熱処理を施したり、あるいは実使用時に金属層が熱を受けることによって、金属層に固溶する酸素や窒素とM-Cr-Al-Y合金層中のAl等とが反応し、金属層とM-Cr-Al-Y合金層との界面にAl等の酸化物や窒化物が生成する。これらAl等の酸化物や窒化物はその内部での元素の拡散係数が小さいことから、より一層拡散バリア層としての機能が向上する。

【0013】そして、拡散バリア層として機能する金属層は、本質的に金属の物性を有する層であるため、基材やM-Cr-Al-Y合金層に対して優れた密着性を示し、また界面にAl等の酸化物や窒化物を生成しても、これらは界面での反応生成物であるため、金属層とM-Cr-Al-Y合金層との密着性を低下させるようなことはない。従って、拡散バリア層界面からの剥離等を有効に防止することができる。

【0014】これらによって、耐熱部材を長時間高温環境に晒されるような条件下で使用したとしても、上記拡散バリア層により基材の高温強度の低下やM-Cr-Al-Y合金層の耐食・耐酸化性の低下等が防止できると共に、拡散バリア層を介在させたことに伴う剥離等が防止できることから、耐熱部材を長期間安定に使用することが可能となる。

【0015】また、本発明の耐熱部材の製造方法によれば、上述した第1の耐熱部材を安定してかつ再現性よく作製することができる。

【0016】本発明の第2の耐熱部材においては、拡散バリア層にNi、CoおよびFeから選ばれる少なくとも1種の元素を主成分とするマトリックス相中に $M_1(A_{1-x}B_x)$ 相が析出した材料を用いており、この拡散バリア層はマトリックス相と析出物相（ $M_1(A_{1-x}B_x)$ 相）との界面での拡散抑止効果により元素の移動距離を長くすることができるため、基材とM-Cr-Al-Y合金

層間での元素移動を抑制することが可能となる。また、拡散バリア層は金属マトリックス相を有しているため、基材や M-Cr-Al-Y合金層に対して優れた密着性を示す。従って、耐熱部材を長時間高温環境に晒されるような条件下で使用したとしても、基材の高温強度の低下や M-Cr-Al-Y合金層の耐食・耐酸化性の低下等が防止できると共に、拡散バリア層を介在させたことに伴う剥離等が防止できることから、耐熱部材を長期間安定に使用することが可能となる。

【0017】

【発明の実施の形態】以下、本発明を実施するための形態について説明する。

【0018】図1は、本発明の第1の耐熱部材の実施形態を示す断面図である。同図において、1は金属基材であり、この金属基材1としてはNi、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする耐熱合金が用いられ、使用用途等に応じて各種公知の耐熱合金を適宜選択して使用することができる。実用上は、IN738、IN738LC、IN939、Mar-M247、RENE80、CM-247、CMSX-2、CMSX-4等のNi基超合金や、FSX-414、Mar-M509等のCo基超合金を用いることが有効である。

【0019】上記金属基材1上には、拡散バリア層として機能する金属層2が形成されており、この金属層2を介してM-Cr-Al-Y合金層3が耐食・耐酸化金属コーティング層として被覆形成されている。これらによって耐熱部材4が構成されている。

【0020】拡散バリア層として形成する金属層2は、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属、あるいはTi、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素とNi、CoおよびFeから選ばれる少なくとも1種の元素との合金を主成分とし、これらに酸素および窒素から選ばれる少なくとも1種が固溶した層からなるものである。

【0021】ここで、Ti、Zr、Hf、V、Ta、Nb等の金属や、これらとNi、Co、Fe等との合金は、酸素や窒素を多く固溶することができる。このような酸素や窒素を多く固溶する金属層2は、Al等の元素の拡散係数が小さいことから、金属基材1とM-Cr-Al-Y合金層3との拡散バリア層として機能する。

【0022】このように、酸素や窒素を多く固溶した金属層2自体も拡散バリア層として機能するが、金属層2成膜後に熱処理を施したり、あるいは熱処理を施さなくとも実使用時に金属層2が熱を受けることによって、上記金属層2に固溶する酸素または窒素とM-Cr-Al-Y合金層3中のAl等とが反応し、図2に示すように、金属層2とM-Cr-Al-Y合金層3との界面にAl等の酸化物または窒化物(Al₂O₃、AlN)5が生成する。これらAl₂O₃やAlN(5)等の物質は、その物質中の元素の拡散係数が小さく、拡散バリア層として有効に利用することができる

すなわち、上述した金属や合金からなる金属層2は、酸素や窒素を多く固溶することができる。一方、耐食・耐酸化性に優れたM-Cr-Al-Y合金は、一般に合金中のAl元素の活量が高く、酸化雰囲気中ではAl₂O₃、窒化雰囲気中ではAlNを生成し易い。従って、酸素や窒素を多く固溶する金属層2とM-Cr-Al-Y合金層3とが接した状態で、熱処理あるいは実使用時の熱を受けると、金属層2中の酸素または窒素とM-Cr-Al-Y合金層3中のAl等とが反応して、Al等の酸化物または窒化物5が界面に生成する。

【0023】これらAl等の酸化物または窒化物5は、その内部での拡散係数が小さく、拡散バリア層として有効に機能することから、耐熱部材4を長時間高温環境に晒されるような条件下で使用したとしても、金属基材1とM-Cr-Al-Y合金層3との間の元素移動を抑制することができる。その結果として、金属基材1の高温強度の低下やM-Cr-Al-Y合金層3の耐食・耐酸化性の低下等が防止でき、耐熱部材4を長期間安定に使用することが可能となる。

【0024】そして、上述した拡散バリア層として機能する金属層2(Al等の酸化物または窒化物5を含む)が従来の拡散バリア層、すなわちAl₂O₃等からなるセラミックス層を直接形成したものと大きく異なる点は、拡散バリア層として機能する金属層2は本質的に金属的物性を有する層(メタリックな層)であり、金属基材1とは金属/金属結合を形成するため、極めて良好な密着性を示す。また、金属層2とM-Cr-Al-Y合金層3との界面に、Al等の酸化物または窒化物5を形成したとしても、これらは金属層2とM-Cr-Al-Y合金層3との界面における反応生成物であるため、金属層2とM-Cr-Al-Y合金層3の結合状態を高める方向に作用し、密着性を低下させるようなことはない。従って、拡散バリア層の存在が耐熱部材4の各層間の密着性を低下させるようなことはなく、拡散バリア層との界面からの剥離等は防止することができる。これによって、耐熱部材4の長寿命化が達成される。

【0025】上述した酸素や窒素を固溶する金属層2における酸素含有量または窒素含有量は、特に限定されるものではないが、少なくとも金属層2自体が金属的な物性を維持し得るような酸素含有量または窒素含有量でなければならない。このような点からは、金属層2の構成元素によっても異なるが、金属層2の酸素含有量または窒素含有量は40at%以下であることが好ましい。金属層2中の酸素量または窒素量が40at%を超えると、金属層2中に酸化物や窒化物が生成し、金属層2本来の金属的特性が低下するおそれがある。また、金属層2とM-Cr-Al-Y合金層3との界面に過剰なAl等の酸化物または窒化物5が生成し、界面剥離等が生じるおそれがある。一方、金属層2中の酸素量または窒素量があまり少ないと、金属層2自体の拡散バリア層としての機能が低下す

ると共に、界面でのAl等の酸化物または窒化物5の生成量が不十分となる。このような点からは、金属層2の酸素含有量または窒素含有量は5at%以上であることが好ましい。

【0026】また、酸素や窒素を固溶する金属層2の厚さは特に限定されるものではないが、良好な拡散バリア効果を安定に得るために5 μ m以上とすることが好ましく、また金属層2自体の剥離等を防止する上で50 μ m以下とすることが好ましい。

【0027】金属層2は、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の金属層に、酸素および窒素から選ばれる少なくとも1種を固溶させることによって、上述したように基本的な拡散バリア層としての機能を得ることができるが、金属基材1側からの元素移動を抑制すると共に、金属基材1との密着性を高めるためには、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素とNi、CoおよびFeから選ばれる少なくとも1種の元素との合金層とすることが好ましい。これらNi、Co、Feの含有量は、金属層2中の酸素や窒素の固溶量に悪影響を及ぼさないように50at%以下とすることが好ましい。また、金属基材1側からの元素移動を安定して抑制するためには10at%以上含有させることが好ましい。

【0028】上述したような酸素や窒素を固溶する金属層2は、例えば以下のようにして形成することができる。

【0029】すなわち、金属基材1の表面に、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素を含有する金属層を、酸素分圧または窒素分圧が0.1~1 $\times 10^4$ Paの雰囲気中で成膜する。ここで、成膜方法としては、減圧プラズマ溶射等のプラズマ溶射法、EB-PVD法、マグネトロンスパッタリング法、CVD法等を適用することができる。

【0030】ここで、プラズマ溶射法は、成膜速度が速く、厚膜を形成する方法として優れている。特に減圧プラズマ溶射法は、緻密な層を成膜することができると共に、過剰な酸化反応等を抑制することができるため、しばしば金属層の成膜に用いられる。例えば、このような減圧プラズマ溶射法を適用すると共に、溶射雰囲気中の酸素分圧または窒素分圧を0.1~1 $\times 10^4$ Paの範囲として、Ti、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の単体金属層、あるいはTi、Zr、Hf、V、TaおよびNbから選ばれる少なくとも1種の元素とNi、CoおよびFeから選ばれる少なくとも1種の元素との合金層を成膜すると、溶射プロセス中に雰囲気内に微量に存在する酸素や窒素が単体金属層や合金層中に固溶して、酸素や窒素を固溶する金属層2を得ることができる。なお、プラズマ溶射法以外の成膜法を適用する場合においても同様である。

【0031】金属層2形成時の酸素分圧または窒素分圧

が0.1Pa未満であると、金属層2中に十分に酸素や窒素を固溶させることができず、上述した拡散バリア効果が低下するおそれがあり、一方1 $\times 10^4$ Paを超えると金属層2自体の酸化や窒化が起り、金属層2の金属的な物性が劣化して金属層2の密着性が低下する。

【0032】酸素や窒素を固溶する金属層2の形成方法は、上述した酸素や窒素を微量含む雰囲気中での成膜に限らず、成膜原料に酸素や窒素を適量含有する物質を使うことによっても、上述したような酸素または窒素を固溶する金属層2を形成することができる。

【0033】上記したような方法で酸素や窒素を固溶する金属層2を形成した後、M-Cr-Al-Y合金層3を1 $\times 10^4$ Pa以下の減圧雰囲気中で成膜する。このM-Cr-Al-Y合金層3の形成にも、減圧プラズマ溶射法、EB-PVD法、マグネトロンスパッタリング法、CVD法等を適用することができる。M-Cr-Al-Y合金層3を成膜する際の雰囲気が1 $\times 10^4$ Paを超えると、成膜時に金属層2表面で酸化等が起り、M-Cr-Al-Y合金層3の密着性が低下する。また、M-Cr-Al-Y合金層3を成膜した後に、このM-Cr-Al-Y合金層3と金属層2との界面に予めAl等の酸化物または窒化物5を形成しておく場合には、例えば窒素やアルゴン等の不活性雰囲気中や減圧雰囲気中で、1000~1500K程度の温度で熱処理を施す。

【0034】上述したM-Cr-Al-Y合金層3は、金属基材1の耐食・耐酸化性コーティングとして機能を得る上で、一般的には0.1~20重量%のAl、10~35重量%のCr、0.1~5重量%のYを含み、残部がNi、CoおよびFeから選ばれる少なくとも1種のM元素から実質的になる組成の合金が用いられる。また、用途によってはM-Cr-Al-Y合金に、Ti、Nb、Hf、Zr、TaおよびWから選ばれる少なくとも1種の添加元素を5重量%以下の範囲で微量添加することも可能である。

【0035】金属基材1表面を酸素や窒素を固溶する金属層2を介してM-Cr-Al-Y合金層3で被覆した部材4を、そのまま耐熱部材として用いてもよいが、使用用途によっては図3に示すように、さらにM-Cr-Al-Y合金層3上にセラミックス層6を遮熱コーティング層として被覆形成し、このような構成の部材7を耐熱部材として用いることもできる。

【0036】上記セラミックス層6には、Si₃N₄、SiC、Al₂O₃、ZrO₂、TiN、AlN、サイアロン等の種々のセラミックス材料を使用することができるが、熱伝導率の低さや熱膨張係数の大きさ等からZrO₂が好適である。また、ZrO₂の相変態を抑止する安定化剤としてはY₂O₃が最も好ましく、特にY₂O₃を8重量%程度含む部分安定化ZrO₂が総合的に最も優れた特性を示す。なお、セラミックス層6は、Alバック法等のAl化処理を施すことによって形成したAl₂O₃層等であってもよい。

【0037】次に、本発明の第2の耐熱部材の実施形態

について、図4および図5を参照して述べる。図4は本発明の第2の耐熱部材の一実施形態を示す断面図であり、11は前述した実施形態と同様な材料からなる金属基材である。この金属基材11上には、拡散バリア層12が形成されており、この拡散バリア層12を介して、前述した実施形態と同様なM-Cr-Al-Y合金層13が被覆形成されている。これらによって耐熱部材14が構成されている。

【0038】上記した拡散バリア層12は、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とするマトリックス相中に、 $M_x(A_{1-x}B_x)_{1-x}$ 相(MはNi、CoおよびFeから選ばれる少なくとも1種の元素を、AはAl、Ti、NbおよびTaから選ばれる少なくとも1種の元素を、BはCr、Mo、W、Hf、ReおよびYから選ばれる少なくとも1種の元素を示し、 a および x は $0.3 \leq a \leq 0.8$ 、 $0 \leq x < 0.5$ である)が析出した材料からなるものである。

【0039】この拡散バリア層12は、従来の拡散バリア層とは異なり、マトリックス相と析出相($M_x(A_{1-x}B_x)_{1-x}$ 相)との界面での拡散抑止効果により元素の移動距離を長くすることによって、金属基材11とM-Cr-Al-Y合金層13間での元素移動を抑制するものである。 $M_x(A_{1-x}B_x)_{1-x}$ 相の a の値が上記範囲外であると、安定な析出相が得られない。このような拡散バリア層12を金属基材11とM-Cr-Al-Y合金層13間に介在させることによって、耐熱部材14を長時間高温環境に晒されるような条件下で使用しても、金属基材11とM-Cr-Al-Y合金層13との間の元素移動を抑制することができる。従って、金属基材11の高温強度の低下やM-Cr-Al-Y合金層13の耐食・耐酸化性の低下等が防止でき、耐熱部材14の長寿命化が図れる。

【0040】上述したような拡散バリア効果を得るために、拡散バリア層12中における $M_x(A_{1-x}B_x)_{1-x}$ 相の析出量(体積率)は、金属基材11中の析出相の体積率より多いことが必要となる。なぜならば、拡散バリア層12中の析出相の体積率が金属基材11中のそれより低いと、マトリックス相中を拡散する元素の経路が短くなり、金属基材11以上の拡散抵抗を持てなくなるため、拡散バリア層12としての機能が得られないためである。通常、例えば金属基材11がNi基合金からなる場合、50~60体積%のNi、Al相等の析出物を含んでおり、このことから考えて拡散バリア層12は50体積%以上の析出相を含むことが好ましい。また、体積率が100%に近いと金属間化合物相特有の脆性的な機械的性質が顕在化するため、析出相の体積率は90%以下とすることが好ましい。

【0041】そして、上述した拡散バリア層12は、金属相をマトリックスとしているため、金属基材1とは金属/金属結合を形成して極めて良好な密着性を示し、また従来の酸化物、窒化物、酸窒化物等の単層からなる拡

散バリア層のような脆さもない。従って、上述した拡散バリア効果に加えて、拡散バリア層12を介在させたことに伴う剥離等が防止できることから、耐熱部材14を長期間安定に使用することが可能となる。

【0042】拡散バリア層12のマトリックス相としては、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とし、これに生成する $M_x(A_{1-x}B_x)_{1-x}$ 相に応じた元素、すなわちAl、Ti、NbおよびTaから選ばれる少なくとも1種の元素、また必要に応じてCr、Mo、W、Hf、ReおよびYから選ばれる少なくとも1種の元素が固溶した固溶体を用いられる。これら固溶元素の量は、 $M_x(A_{1-x}B_x)_{1-x}$ 相の析出量に応じて適宜設定される。このように、拡散バリア層12のマトリックス相は、Ni、CoおよびFeから選ばれる少なくとも1種の元素を主成分とする固溶体であればよいが、金属基材1との整合性、金属基材1での異種相の生成を防止する観点から、金属基材1がNi基合金であればNiを主成分とし、またCo基合金であればCoを主成分とすることが好ましい。

【0043】また、析出相は、Ni、CoおよびFeから選ばれる少なくとも1種の元素(M元素)とAl、Ti、NbおよびTaから選ばれる少なくとも1種の元素(A元素)とを所定の比率で含むものであればよいが、例えばNiを主成分とするマトリックス相を用いる場合には $Ni_{0.75}(Al,Ti,Nb)_{0.25}$ 、 $(Ni_3(Al,Ti,Nb))$ 、 $Ni_{0.5}Al_{0.5}$ 、 $(NiAl)$ 、 $Ni_{0.25}Al_{0.75}$ 、 $(NiAl_3)$ 等の金属間化合物相、またCoを主成分とするマトリックス相を用いる場合には $Co_{0.5}Al_{0.5}$ 、 $(CoAl)$ 等の金属間化合物相が、熱的・化学的安定性等の点から好ましい。また、析出相の安定性を高めたり、マトリックス相との整合性を乱して元素拡散に対する抵抗性を向上させるために、Cr、Mo、W、Hf、ReおよびYから選ばれる少なくとも1種の元素(B元素)で、A元素の一部を置換することができる。ただし、B元素量はA元素量を超えないようにする。

【0044】ところで、M-Cr-Al-Y合金層13は、一般にM元素がNiの場合にはNiAl相のようなβ相、またM元素がCoの場合にもCoAl相のようなβ相を主として含んでいる。従って、拡散バリア層12中の析出相がβ相の場合には、その体積率をM-Cr-Al-Y合金層13中の体積率より多くすることが好ましい。これによって、M-Cr-Al-Y合金層13からのAl等の移動をより一層効果的に抑制することができる。一方、金属基材1はNi₃Al相等のγ'相を主として含んでいることから、拡散バリア層12中の析出相をγ'相とすることも効果的である。すなわち、拡散バリア層12の析出物組成を金属基材11に近付けることによって、M-Cr-Al-Y合金層13からのAl等の移動を効果的に抑制することができる。

【0045】上述した拡散バリア層12の厚さは、特に限定されるものではないが、良好な拡散バリア効果を安定に得るために1μm以上とすることが好ましく、また

拡散バリア層12自体の剥離等を防止する上で200 μ m以下とすることが好ましい。また、拡散バリア層12の形成方法には、プラズマ溶射法、HVOF法、PVD法、CVD法等の各種成膜プロセスを適用することができ、特に成膜速度や材料選択の幅が広いこと等からプラズマ溶射法が有効である。プラズマ溶射法の中でも、減圧雰囲気中で溶射プロセスを行う減圧プラズマ溶射法(VPS法)が好ましく、これによってプロセス時の酸化が抑制できると共に、緻密な被覆層を形成することができる。M-Cr-Al-Y合金層13の形成方法についても同様である。金属基材11表面を拡散バリア層12を介してM-Cr-Al-Y合金層13で被覆した部材14を、そのまま耐熱部材として用いてもよいが、前述した実施形態と同様に、使用用途によっては図5に示すように、さらにM-Cr-Al-Y合金層13上にセラミックス層15を遮熱コーティング層として被覆形成し、このような構成の部材16を耐熱部材として用いることもできる。セラミックス層15の構成は前述した実施形態と同様とすることが好ましい。

【0046】

【実施例】次に、本発明の具体的な実施例について説明する。

【0047】実施例1

Ni基超合金CM-247からなる丸棒材料の表面に、約100Paの減圧大気中で減圧プラズマ溶射法により厚さ10 μ mのTi層を成膜した。この際の溶射雰囲気中の酸素分圧は約25Paである。次いで、同一チャンバ内で厚さ150 μ mのNiCoCrAlY層(Ni-23%Co-17%Cr-12%Al-0.5%Y(重量%))を成膜した。上記Ti層中の酸素量を測定したところ33at%あった。

【0048】このようにして得た耐熱部材にAr雰囲気炉中で1273Kで1000時間の熱処理を施した。この熱処理後の試料に、1173Kで250MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からTi層、Al₂O₃層、NiCoCrAlY層の順に存在していた。

【0049】また、本発明との比較例として、Ni基超合金CM-247からなる丸棒材料の表面に減圧プラズマ溶射法により直接同組成のNiCoCrAlY層を成膜した試料に、上記実施例1と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、80時間経過した時点で破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相(γ' 相)の消失が認められ、さらにCr-Wからなる脆弱な生成相が観察された。

【0050】実施例2

Ni基超合金IN738からなる丸棒材料の表面に、約10Paの減圧大気中で減圧プラズマ溶射法により厚さ15 μ mのTi-50at%Ni層を成膜した。この際の溶射雰囲気中の酸素分

圧は約2Paである。次いで、同一チャンバ内で厚さ100 μ mのCoNiCrAlY層(Co-32%Ni-21%Cr-8%Al-0.5%Y(重量%))を成膜した。上記Ti-50at%Ni層中の酸素量を測定したところ15at%あった。

【0051】このようにして得た耐熱部材に実施例1と同一条件で熱処理を施した後、1123Kで300MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からTi-Ni-O層、Al₂O₃層、CoNiCrAlY層の順に存在していた。

【0052】また、本発明との比較例として、Ni基超合金IN738からなる丸棒材料の表面に、減圧プラズマ溶射法により直接同組成のCoNiCrAlY層を成膜した試料に、上記実施例2と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、60時間経過の後に破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相(γ' 相)の消失が認められ、さらにCr-Wからなる脆弱な生成相が観察された。

20 【0053】実施例3

Ni基超合金CM-247からなる丸棒材料の表面に、約1000Paの減圧大気中で減圧プラズマ溶射法により厚さ15 μ mのTa-50at%Ni層を成膜した。この際の溶射雰囲気中の酸素分圧は約200Paである。次いで、同一チャンバ内で厚さ120 μ mのCoNiCrAlY層(実施例2と同組成)を成膜した。上記Ta-50at%Ni層中の酸素量を測定したところ10at%あった。

30 【0054】このようにして得た耐熱部材に実施例1と同一条件で熱処理を施した後、1173Kで250MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からTa-Ni層、Al₂O₃層、CoNiCrAlY層の順に存在していた。

40 【0055】また、本発明との比較例として、Ni基超合金CM-247からなる丸棒材料の表面に、減圧プラズマ溶射法により直接同組成のCoNiCrAlY層を成膜した試料に、上記実施例3と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、85時間経過の後に破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相(γ' 相)の消失が認められた。

【0056】実施例4

Co基超合金FSX-414からなる丸棒材料の表面に、約50Paの減圧大気中で減圧プラズマ溶射法により厚さ15 μ mのNb-50at%Co層を成膜した。この際の溶射雰囲気中の酸素分圧は約5Paである。次いで、同一チャンバ内で厚さ100 μ mのCoNiCrAlY層(実施例2と同組成)を成膜した。上記Nb-50at%Co層中の酸素量を測定したところ5at%あった。

50 【0057】このようにして得た耐熱部材に実施例1と

同一条件で熱処理を施した後、1023Kで200MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からNb-Co層、 Al_2O_3 層、NiCoCrAlY層の順に存在していた。

【0058】また、本発明との比較例として、Co基超合金FSX-414からなる丸棒材料の表面に、減圧プラズマ溶射法により直接同組成のNiCoCrAlY層を成膜した試料に、上記実施例4と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、50時間経過の後に破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相（ γ' 相）の消失が認められた。

【0059】実施例5

Ni基超合金QM-247からなる丸棒材料の表面に、約1Paの酸素雰囲気中でEB-PVD法により厚さ5 μm のZr-Nb層を成膜した。次いで、同一チャンバ内で厚さ130 μm のNiCoCrAlY層（実施例1と同組成）を成膜して、金属被覆層を形成した。さらにその上に、EB-PVD法で Y_2O_3 安定化ZrO₂層を200 μm の厚さで形成した。上記Zr-Nb層中の酸素量を測定したところ20at%であった。

【0060】このようにして得た耐熱部材に実施例1と同一条件で熱処理を施した後、1173Kで250MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からZr-Nb層、 Al_2O_3 層、NiCoCrAlY層の順に存在していた。

【0061】また、本発明との比較例として、Ni基超合金QM-247からなる丸棒材料の表面に、EB-PVD法により直接同組成のNiCoCrAlY層を成膜し、さらにその上に Y_2O_3 安定化ZrO₂層を形成した試料に、上記実施例5と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、90時間経過の後に破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相（ γ' 相）の消失が認められ、さらにCr-Wからなる脆弱な生成相が観察された。

【0062】実施例6

Ni基超合金QM-247からなる丸棒材料の表面に、約1Paの酸素雰囲気中でEB-PVD法により厚さ8 μm のTi-Nb層を成膜した。次いで、同一チャンバ内で厚さ80 μm のNiCoCrAlY層（実施例1と同組成）を成膜して、金属被覆層を形成した。さらにその上に、EB-PVD法で Y_2O_3 安定化ZrO₂層を250 μm の厚さで形成した。上記Ti-Nb層中の酸素量を測定したところ10at%であった。

【0063】このようにして得た耐熱部材に実施例1と同一条件で熱処理を施した後、1173Kで250MPaの応力下でクリープ試験を行ったところ、100時間保持しても破

断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からTi-Nb-O層、NiCoCrAlY層の順に存在していた。

【0064】また、本発明との比較例として、Ni基超合金QM-247からなる丸棒材料の表面に、EB-PVD法により直接同組成のNiCoCrAlY層を成膜し、さらにその上に Y_2O_3 安定化ZrO₂層を形成した試料に、上記実施例6と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、90時間経過の後に破断した。この試料を切断して断面観察を行ったところ、界面近傍の基材内では強化相（ γ' 相）の消失が認められ、さらにCr-Wからなる脆弱な生成相が観察された。

【0065】実施例7

Ni基超合金QM-247からなる丸棒材料の表面に、約10Paの減圧大気中で減圧プラズマ溶射法により厚さ20 μm のNb-30at%Ni層を成膜した。この際の溶射雰囲気中の酸素分圧は約4Paである。次いで、同一チャンバ内で厚さ100 μm のNiCoCrAlY層（実施例1と同組成）を成膜した。上記Nb-30at%Ni層中の酸素量を測定したところ5at%であった。

【0066】このようにして得た耐熱部材に実施例1と同一条件で熱処理を施した後、1123Kで300MPaの応力下でクリープ試験を行ったところ、100時間保持しても破断は見られなかった。また、この試料を切断して断面観察を行ったところ、基材側からNb-Ni-O層、 Al_2O_3 層、NiCoCrAlY層の順に存在していた。

【0067】また、本発明との比較例として、Ni基超合金QM-247からなる丸棒材料の表面に、EB-PVD法により厚さ2 μm の Al_2O_3 層を成膜し、さらに実施例7と同組成のNiCoCrAlY層を成膜した試料に、上記実施例7と同一条件で熱処理を施した。この熱処理後の試料のクリープ試験を同一条件で行ったところ、80時間経過の後に破断した。この試料を切断して断面観察を行ったところ、 Al_2O_3 層と基材との界面および Al_2O_3 層とNiCoCrAlY層との界面から剥離が生じており、この剥離が破断の原因となっていることが分かった。

【0068】実施例8

Ni基超合金IN738からなる基材を20×20×3mmの寸法に加工し、その表面にNi-10%Co-17%Al合金（重量%）を溶射原料として用いて、減圧プラズマ溶射法で厚さ50 μm の拡散バリア層を形成した。次いで、この拡散バリア層上に厚さ150 μm のNiCoCrAlY層（Ni-23%Co-17%Cr-12%Al-0.5%Y（重量%））を、減圧プラズマ溶射法によって被覆形成した。上記拡散バリア層は、体積率71%のNi、Al相を有していた。また、基材中のNi、Al相の体積率は52%であった。

【0069】また、本発明との比較例として、上記実施例8と同寸法に加工したNi基超合金IN738からなる基材表面に、上記実施例8と同組成のNiCoCrAlY層を厚さ2

00 μ mで直接被覆形成した。

【0070】これらの各試料を1173K \times 5000hの大気中酸化試験に暴露した。試験後、各試料の断面をSEMで観察した結果、比較例の試料では表面から36 μ mの厚さで酸化物層が成長していたが、実施例8による試料では13 μ m程度であった。また、NiCoCrAlY層の組織を観察したところ、十分なAl濃度がある初期状態ではいずれもNiを主成分とするマトリックス相にNiAl相が析出した構成であったが、熱処理後には、比較例の試料では熱処理によりAlが基材側に拡散した結果、NiAl相は完全に消失していた。一方、実施例8の試料では、NiCoCrAlY層の表面近傍では酸化物の生成によってAlが消費され、NiAl相は消失していたが、表面から23 μ m以上の内部は初期と同様に、NiとNiAl相とから構成されており、本発明による拡散バリア層が十分な拡散抑制効果を有することが分かった。さらに、基材での異種相の厚さを測定したところ、比較例の試料では127 μ mであったのに対して、実施例8の試料では23 μ mとなっており、基材の強度低下の抑止にも本発明による拡散バリア層が有効に寄与することが分かった。

【0071】実施例9

Ni基超合金IN738からなる基材を20 \times 20 \times 3mmの寸法に加工し、その表面にNi-10%Co-17%Al合金(重量%)を溶射原料として用いて、減圧プラズマ溶射法で厚さ20 μ mの拡散バリア層を形成した。次いでこの拡散バリア層上に厚さ100 μ mのNiCoCrAlY層(実施例8と同組成)を、減圧プラズマ溶射法によって被覆形成した。さらに最表面にZrO₂-8wt%Y₂O₃を200 μ m被覆形成した。基材中のNi₃Al相の体積率は55%であり、拡散バリア層のNi₃Al相の体積率は74%であった。また、本発明との比較例として、上記実施例9と同寸法に加工したNi基超合金IN738からなる基材表面に、上記実施例9と同組成のNiCoCrAlY層を厚さ100 μ mで直接被覆形成し、さらに最表面にZrO₂-8wt%Y₂O₃を200 μ m被覆形成した。

【0072】これらの試料を1173K \times 5000hの大気中酸化試験に暴露した。試験後、各試料の断面をSEMで観察した結果、比較例の試料ではNiCoCrAlY層内部にセラミックス層との界面から28 μ mの厚さで酸化物層が成長していたが、実施例9の試料では9 μ m程度であった。また、NiCoCrAlY層の組織を観察したところ、十分なAl濃度がある初期状態ではいずれもNiを主成分とするマトリックス相にNiAl相が析出した構成であったが、熱処理後には、比較例の試料ではAlが基材に拡散した結果、NiAl相は完全に消失していた。一方、実施例9の試料では、セラミックス層/NiCoCrAlY層の界面近傍では酸化物の生成によりAlが消費され、NiAl相は消失していたが、界面から13 μ m以上内部では初期と同様に、NiとNiAl相とから構成されており、本発明の拡散バリア層が十分な拡散抑制効果を有することが分かった。さらに、基材での異種相の厚さを測定したところ、比較例では108 μ m

であったが、実施例9では16 μ mとなっており、基材の強度低下の抑止にも本発明の拡散バリア層が有効に寄与することが分かった。

【0073】実施例10

単結晶Ni基超合金CMSX-2からなる基材を20 \times 20 \times 3mmの寸法に加工し、その表面にNi-15%Al-17%Cr合金(重量%)を溶射原料として用いて、減圧プラズマ溶射法で厚さ20 μ mの拡散バリア層を形成した。次いで、CoNiCrAlY層(Co-32%Ni-21%Cr-8%Al-0.5%Y(重量%))を厚さ80 μ mで被覆形成した。この試料に1323K \times 16h+1123K \times 48hの熱処理を施した。断面のSEM観察の結果、各被覆層とも γ 相(Ni固溶体)をマトリックスとして、 β 相(NiAl相)が析出していたが、この β 相の体積率はCoNiCrAlY層では44%、拡散バリア層では69%であった。また基材は γ 相と γ' 相(Ni₃Al相)から構成され、 γ' 相の体積率は52%であった。

【0074】また、本発明との比較例として、中間にNi-Al-Cr層を形成しない以外は同一プロセスで試料を作製した。この試料の各部における相構成は、CoNiCrAlY層が γ 相マトリックス中に体積率46%の β 相を有し、基材は γ 相中に体積率56%の γ' 相を有していた。

【0075】これら各試料を1173K \times 5000hの静止大気中酸化試験に供した。試験後、各試料の断面観察を行った結果、比較例の試料では被覆層から β 相が完全に消失し、表面酸化層も表面から37 μ mの厚さまで成長していた。これに対して、実施例10の試料では、CoNiCrAlY層内の β 相は拡散バリア層との界面から14 μ mまでは消失していたが、それ以外の部位では残存し、表面酸化層の厚さは5 μ m程度に抑制されていた。以上の結果から、本発明の拡散バリア層が耐酸化性を長時間持続させる効果を有することが明かである。

【0076】実施例11

Ni基超合金IN-738LCからなる基材の表面に、その表面にNi-14%Al合金(重量%)を溶射原料として用いて、減圧プラズマ溶射法で厚さ20 μ mの拡散バリア層を形成した。次いで、NiCoCrAlY層(実施例8と同一組成)を厚さ120 μ mで被覆形成した。また、本発明との比較例として、拡散バリア層を形成しない以外は同一構成の試料を作製した。その後、これらの試料に1393K \times 2h+1123K \times 24hの熱処理を施した。

【0077】熱処理後、各試料の断面のSEM観察を行い、各部位の相構成を調べた。その結果、実施例および比較例共に基材は γ + γ' 相からなり、 γ' 相の体積率は実施例が42%、比較例が44%であった。また、NiCoCrAlY層はいずれの試料とも γ + β 相から構成され、 β 相の体積率は実施例が51%、比較例が49%であった。実施例における拡散バリア層は、 γ 相をマトリックスとし、体積率73%の γ' 相が析出した構成になっていた。

【0078】これら実施例および比較例による各試料を1173K \times 5000hの大気中酸化試験に供した。試験後、各

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試料の断面をSEM観察した結果、比較例ではNiCoCrAlY層中のβ相は基材界面から100μmまで完全に消失し、また残部の体積率も11%以下となっていた。この被覆層の耐酸化性はAlの消失によって著しく低下し、表面から12μmの厚さまで表面酸化膜が成長していた。これに対して、実施例による試料では、拡散バリア層から14μmの厚さまではβ相が消失していたが、残部はβ相が46%以上存在してしており、これらの耐酸化効果によって表面酸化物層は3μmまでしか成長していなかった。以上の結果から、本発明の拡散防止層が耐酸化性の長時間維持に効果を有することが分かった。

【0079】実施例12

Co基超合金FSX-414からなる基材の表面に、Co-17%Cr-24%Al合金（重量%）を溶射原料として用いて、減圧ブラズマ溶射法で厚さ23μmの拡散バリア層を形成した。次いで、CoNiCrAlY層（実施例10と同一組成）を厚さ130μmで被覆形成した。また、本発明との比較例として、拡散バリア層を形成しない以外は同一構成の試料を作製した。その後、これらの試料に1423K×4h+1198K×10h+813K×24hの熱処理を施した。これら各試料の断面組織をSEMにより観察して各層の構成を調べた結果、CoNiCrAlY層は実施例および比較例共にγ相（Co固溶体）マトリックスとβ相（CoAl相）とから構成され、β相の体積率は実施例では47%、比較例では43%であった。また、拡散バリア層もγ相とβ相とからなり、β相の体積率は72%であった。

【0080】これらの各試料を1173K×5000hの静止大気中酸化試験に供した結果、比較例の試料ではCoNiCrAlY層内のβ相が完全に消失し、表面酸化物層は25μmまで成長していた。一方、実施例の試料ではCoNiCrAlY層のβ相は拡散バリア層界面から17μmまで消失していたが、残部は38%以上存在しており、また表面酸化物層は7μmまでしか成長していなかった。

【0081】実施例13

単結晶Ni基超合金CMSX-2からなる基材の表面に、Ni-13%Al合金（重量%）を溶射原料として用いて、減圧ブラズマ溶射法で厚さ23μmの拡散バリア層を形成した。次いでNiCoCrAlY層（実施例8と同一組成）を厚さ120μmで被覆形成した。さらに、この表面にZrO₂-8wt%Y₂O₃層を大気ブラズマ溶射法で厚さ230μm被覆形成した。また本発明との比較例として、拡散バリア層を形成しない以外は同一構成の試料（ただし、NiCoCrAlY層を厚さは130μm、ZrO₂-8wt%Y₂O₃層の厚さは240μmとした）を作製した。これら各試料の断面のSEM観察の結果、NiCoCrAlY層はγ相（Ni固溶体）とβ相（NiAl相）とからなり、β相の体積率は実施例では53%、比較例では50%であった。また基材はγ相とγ'相（Ni₃Al相）とからなり、γ'相の体積率は実施例では61%、比較例では59%であった。拡散バリア層はγ相とγ'相から構成され、γ'相の体積率は87%であった。これら各

試料を1173K×5000hの静止大気中酸化試験に供した。試験後、断面のSEM観察を行った結果、比較例ではNiCoCrAlY層中のβ相が基材界面から90μmまで完全に消失し、ZrO₂層との界面から14μmの厚さまで酸化物層が形成していた。これに対して実施例の試料では、NiCoCrAlY層内のβ相は拡散防止層界面から17μmまでしか消失せず、残部も19%以上の体積率でβ相が残っていた。またZrO₂層との界面側の酸化物層の厚さも3μm程度で、耐酸化性が格段に改善されていた。

【0082】実施例14

単結晶Ni基超合金CMSX-2からなる基材の表面に、Ni-17%Ti-5%Al合金（重量%）を溶射原料として用いて、減圧ブラズマ溶射法で厚さ25μmの拡散バリア層を形成した。次いで、NiCoCrAlY層（実施例8と同一組成）を厚さ130μmで被覆形成した。さらに、その表面にZrO₂-8wt%Y₂O₃層を大気ブラズマ溶射法で厚さ210μm被覆形成した。また、本発明との比較例として、拡散バリア層を形成しない以外は同一構成の試料を作製した。これら各試料に1323K×16h+1123K×48hの熱処理を施した後、断面のSEM観察を行った結果、基材はγ相（Ni固溶体）とγ'相（Ni₃Al）とからなり、γ'相の体積率は実施例では55%、比較例では54%であった。また、NiCoCrAlY層はγ相とβ相とからなり、β相の体積率は実施例では43%、比較例では46%であった。さらに、拡散バリア層はγ相とη相（Ni₃Ti相）とからなり、η相の体積率は74%であった。

【0083】これらの各試料を1173K×5000hの静止大気中酸化試験に供した。試験後、断面のSEM観察を行った結果、比較例の試料ではNiCoCrAlY層中のβ相は完全に消失し、ZrO₂層との界面に19μmの酸化物層が形成していたのに対し、実施例の試料ではNiCoCrAlY層中のβ相は拡散バリア層界面から13μmまでは消失していたが、それ以外の部位では12%以上残存しており、さらにZrO₂層との界面側の酸化物層の厚さも4μm程度であった。以上の結果から、本発明が耐酸化性の維持に効果を有することが明らかとなった。

【0084】

【発明の効果】以上説明したように、本発明の耐熱部材によれば、耐食・耐酸化性を長時間維持し、かつ基材の高温強度の低下が抑制できると共に、各層間の剥離等も防止できることから、耐熱部材の信頼性と寿命を格段に向上させることが可能となる。従って、例えばガスタービン翼のように熱応力と酸化、さらには腐食が重畳して作用するような環境下であっても、優れた耐食・耐酸化性ならびに高温強度を長時間にわたって維持することが可能な耐熱部材を提供することができる。

【図面の簡単な説明】

【図1】 本発明の第1の耐熱部材の一実施形態を示す断面図である。

【図2】 図1に示す耐熱部材の熱処理語の状態または

実使用状態を示す断面図である。

【図3】 図1に示す耐熱部材にセラミックス層を被覆形成した状態を示す断面図である。

【図4】 本発明の第2の耐熱部材の一実施形態を示す断面図である。

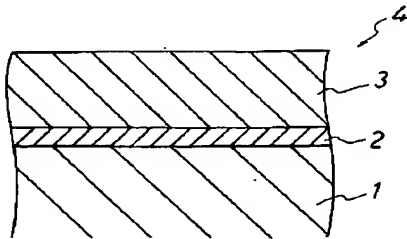
【図5】 図4に示す耐熱部材にセラミックス層を被覆形成した状態を示す断面図である。

【符号の説明】

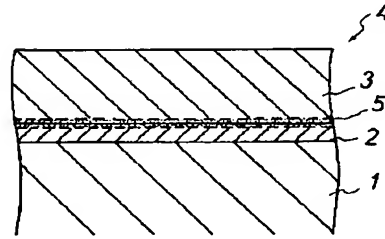
*

- * 1、11……金属基材
 2……酸素や窒素を固溶する金属層
 3、13…… M-Cr-Al-Y合金層
 4、7、14、16……耐熱部材
 5……Al等の酸化物または窒化物
 12……拡散バリア層
 15……セラミックス層

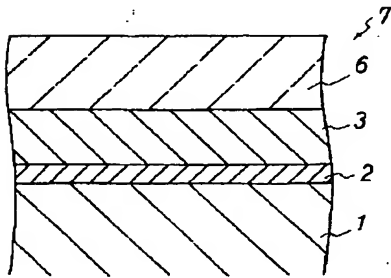
【図1】



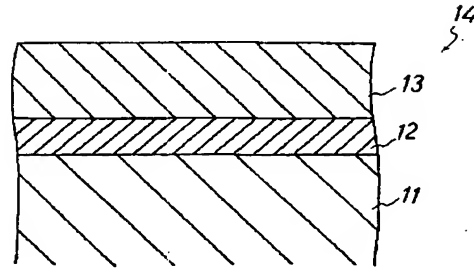
【図2】



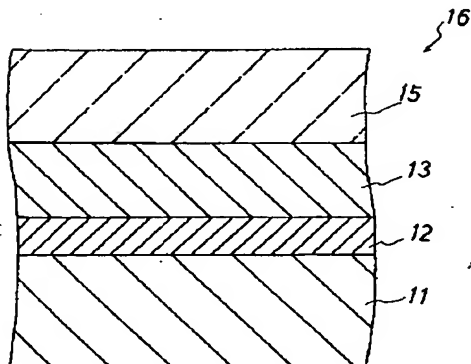
【図3】



【図4】



【図5】



フロントページの続き

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CLAIMS

[Claim(s)]

[Claim 1] It is as being chosen out of nickel, Co, and Fe that it is few. The base material which consists of an alloy which uses one sort of elements as a principal component, Covering formation was carried out through the diffusion barrier layer on said base material front face. In the heat-resistant member possessing a M-Cr-aluminum-Y alloy layer (however, it is indicated with M being chosen from nickel, Co, and Fe that a 1 sort element is few) Said diffusion barrier layer is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb as it is few. It is as using one sort of metals as a principal component, and being chosen out of oxygen and nitrogen that it is few. Heat-resistant member characterized by having the metal layer in which one sort dissolved.

[Claim 2] It is as being chosen out of nickel, Co, and Fe that it is few. The base material which consists of an alloy which uses one sort of elements as a principal component, Covering formation was carried out through the diffusion barrier layer on said base material front face. In the heat-resistant member possessing a M-Cr-aluminum-Y alloy layer (however, it is indicated with M being chosen from nickel, Co, and Fe that a 1 sort element is few) Said diffusion barrier layer is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb as it is few. One sort of elements, and nickel, It is as being chosen out of Co and Fe that it is few. It is as using an alloy with one sort of elements as a principal component, and being chosen out of oxygen and nitrogen that it is few. Heat-resistant member characterized by having the metal layer in which one sort dissolved.

[Claim 3] It is as being chosen out of nickel, Co, and Fe that it is few. The base material which consists of an alloy which uses one sort of elements as a principal component, Covering formation was carried out through the diffusion barrier layer on said base material front face. In the heat-resistant member possessing a M-Cr-aluminum-Y alloy layer (however, it is indicated with M being chosen from nickel, Co, and Fe that a 1 sort element is few) Said diffusion barrier layer is as being chosen out of nickel, Co, and Fe as it is few. In the matrix phase used as a principal component, one sort of elements a $Ma1(A1-xBx)$ -a phase (however, M -- nickel --) It is as being chosen out of Co and Fe that it is few. A one sort of elements aluminum, It is as being chosen out of Ti, Nb, and Ta that it is few. B one sort of elements Cr, Mo, and W, Hf and Re -- and -- it is chosen out of Y -- at least -- One sort of elements are shown. a -- and -- $x \ 0.3 \leq a \leq 0.8$ and $0 \leq x < 0.5$ -- it is -- from the depositing ingredient -- becoming -- and the above Heat-resistant member characterized by there being more amounts of deposits (rate of the volume) of a $Ma1(A1-xBx)$ -a phase than the rate of the volume of the deposit phase in said base material.

[Claim 4] In claim 1 and a heat-resistant member according to claim 2 or 3, it describes above further. Heat-resistant member characterized by having the ceramic layer by which covering formation was carried out on a M-Cr-aluminum-Y alloy layer front face.

[Claim 5] It is as being chosen out of nickel, Co, and Fe that it is few. On the base material front face which consists of an alloy used as a principal component, one sort of elements It is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb that it is few. Oxygen tension or a nitrogen partial pressure the metal layer containing one sort of elements The process which forms membranes in the ambient atmosphere of $0.1 - 1 \times 10^4$ Pa, The manufacture approach of the heat-resistant member characterized by having the process which forms a M-Cr-aluminum-Y alloy layer (however, it is indicated with M being chosen from nickel, Co, and Fe that a 1 sort element is few) in the reduced pressure ambient atmosphere below 1×10^4 Pa on said metal layer.

[Translation done.]

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 DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the heat-resistant member suitable like the component of the ** and the stationary blade of a gas turbine for the ingredient with which the high temperature strength of long duration, oxidation resistance, and corrosion resistance are demanded under hot environments, and its manufacture approach.

[0002]

[Description of the Prior Art] The property of a high level, for example, high temperature strength, elevated-temperature anticorrosion, oxidation resistance, etc. are further demanded of the ingredient used for configuration components with elevated-temperature-izing of the device service temperature which aimed at efficient-ization of the elevated-temperature device represented by the gas turbine for the object for a generation of electrical energy, or engines. For this reason, the technique of performing anticorrosion and anti-oxidation metal coating which consists of M-Cr-aluminum-Y alloys (M=nickel, Co, Fe, etc.) etc. is developed, and it is already widely applied to the front face of the superalloy base material of nickel radical of high intensity, or Co radical as an indispensable technique in **, the stationary blade, etc. of a gas turbine. Moreover, in the flow of the further elevated-temperature-izing, the front face of anticorrosion and an anti-oxidation metal coating layer is coated with a ceramic layer with the low heat conductivity, and the thermal-barrier-coating technique which protects an inside metallic material is also being put in practical use.

[0003] By the way, since it has mainly been carried out from a viewpoint the corrosion resistance which is the original purpose, and oxidation-resistant, ingredient development of the conventional metal coating is the alloy base material of nickel radical or Co radical. Ingredient presentations with the metal coating layer which consists of a M-Cr-aluminum-Y alloy will differ remarkably, and element migration will produce them in the base material / metal coating layer interface which touches the bottom of operation of the gas turbine of long duration etc. directly as the result. Protection nature oxide layer formation elements, such as aluminum and Cr, were drained from the metal coating layer with this element migration, the anticorrosion and the oxidation resistance of a metal coating layer fall, or the problem of high temperature strength falling by generation of the different-species phase inside a base material is caused.

[0004] In order to solve the problem accompanying the element migration by the base material / metal coating layer interface which was mentioned above, forming the diffusion barrier layer which controls element diffusion between a base material and a metal coating layer is examined.

Conventionally, as such a diffusion barrier layer, although to form the oxide layer which uses small aluminum and small Ti of a diffusion coefficient of an element in the interior as a principal component, a nitride layer, an acid nitride layer, etc. using the membrane formation approaches, such as a CVD method, is tried, the problem that the adhesion in the interface of a diffusion barrier layer and a base material or the interface of a diffusion barrier layer and a metal coating layer is bad, and exfoliation tends to take place by these interfaces has arisen. The exfoliation by this interface is the life fall factor of a heat-resistant member.

[0005]

[Problem(s) to be Solved by the Invention] Although to form a diffusion barrier layer is tried in order to solve the problem accompanying the element migration by the base material / metal coating layer

interface in the heat-resistant member which applied metal coating, and also the heat-resistant member which gave thermal barrier coating as mentioned above. It had the problem of the diffusion barrier layer which carried out direct covering formation of conventional oxide, a nitride, the acid nitride, etc. having bad adhesion with a base material metallurgy group coating layer, and exfoliation having arisen from these interfaces and reducing a member life.

[0006] While making it possible to fully control degradation accompanying the element migration by the base material / metal coating layer interface in the conventional refractory coating member from such a thing, to raise the adhesion of the diffusion barrier layer itself was made into the technical problem.

[0007] This invention was made in order to cope with such a technical problem, it raises the adhesion between each class, controls interfacial peeling, and aims at offering the heat-resistant member which attained reinforcement while it makes it possible to fully control the element migration between a base material / metal coating layer over long duration.

[0008]

[Means for Solving the Problem] the 1st heat-resistant member in this invention is chosen from nickel, Co, and Fe, as indicated to claim 1 -- at least -- M-Cr-aluminum-Y alloy layer. Covering formation was carried out through the diffusion barrier layer on the base material which consists of an alloy which uses one sort of elements as a principal component, and said base material front face. (however, M is chosen from nickel, Co, and Fe -- at least -- -- one sort of elements are shown.) the following -- being the same -- the heat-resistant member to provide -- setting -- said diffusion barrier layer -- Ti -- It is as being chosen out of Zr, Hf, and V, Ta and Nb that it is few. It is as using one sort of metals as a principal component, and being chosen out of oxygen and nitrogen that it is few. As indicated to having the metal layer in which one sort dissolved, or claim 2 Said diffusion barrier layer is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb as it is few. One sort of elements, and nickel, It is as being chosen out of Co and Fe that it is few. It is as using an alloy with one sort of elements as a principal component, and being chosen out of oxygen and nitrogen that it is few. It is characterized by having the metal layer in which one sort dissolved.

[0009] The 2nd heat-resistant member in this invention is as being chosen out of nickel, Co, and Fe as indicated to claim 3 as it is few. The base material which consists of an alloy which uses one sort of elements as a principal component, Covering formation was carried out through the diffusion barrier layer on said base material front face. In the heat-resistant member possessing a M-Cr-aluminum-Y alloy layer said diffusion barrier layer It is as being chosen out of nickel, Co, and Fe that it is few. In the matrix phase used as a principal component, one sort of elements a $Ma_1(A_{1-x}B_x)$ -a phase (however, M -- nickel --) It is as being chosen out of Co and Fe that it is few. A one sort of elements aluminum, It is as being chosen out of Ti, Nb, and Ta that it is few. B one sort of elements Cr, Mo, and W, Hf and Re -- and -- it is chosen out of Y -- at least -- One sort of elements are shown. a -- and -- x -- $0.3 \leq a \leq 0.8$ and $0 \leq x \leq 0.5$ -- it is -- from the depositing ingredient -- becoming -- and the above It is characterized by there being more amounts of deposits (rate of the volume) of a $Ma_1(A_{1-x}B_x)$ -a phase than the rate of the volume of the deposit phase in said base material.

[0010] The heat-resistant member of this invention is further described above, as indicated to claim 4. You may have the ceramic layer by which covering formation was carried out on the M-Cr-aluminum-Y alloy layer front face.

[0011] Moreover, as indicated to claim 5, the manufacture approach of the heat-resistant member of this invention It is as being chosen out of nickel, Co, and Fe that it is few. On the base material front face which consists of an alloy used as a principal component, one sort of elements It is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb that it is few. Oxygen tension or a nitrogen partial pressure the metal layer containing one sort of elements The process which forms membranes in the ambient atmosphere of $0.1 - 1 \times 10^4$ Pa, On said metal layer M-Cr-aluminum-Y alloy layer It is characterized by having the process which forms membranes in the reduced pressure ambient atmosphere below 1×10^4 Pa.

[0012] It is that it is few as a diffusion barrier layer is chosen from Ti, Zr, Hf, and V, Ta and Nb in the 1st heat-resistant member of this invention. It is as being chosen out of one sort of metals or these, and nickel, Co and Fe that it is few. It has the metal layer which uses an alloy with one sort of

elements as a principal component. The metal layer which many alloys of these, nickel, Co, Fe, etc., etc. can dissolve oxygen and nitrogen, and dissolve this oxygen and nitrogen is a base material since the diffusion coefficient of elements, such as aluminum in that interior, is small. It functions as a diffusion barrier layer with a M-Cr-aluminum-Y alloy layer. [metals, such as Ti, Zr, Hf, and V Ta, Nb,] Moreover, oxygen and nitrogen which dissolve in a metal layer when it heat-treats in the above-mentioned metal layer or a metal layer receives heat at the time of real use aluminum in a M-Cr-aluminum-Y alloy layer etc. reacts, and it is a metal layer. Oxides and nitrides, such as aluminum, generate to an interface with a M-Cr-aluminum-Y alloy layer. From the diffusion coefficient of the element in the interior being small, the function of nitrides [, such as these aluminum, / oxide or nitrides] as a diffusion barrier layer improves further.

[0013] And since it is the layer which essentially has metallic physical properties, the metal layer which functions as a diffusion barrier layer is a base material. Since these are the resultants in an interface even if the adhesion which was excellent to the M-Cr-aluminum-Y alloy layer is shown and it generates oxides and nitrides, such as aluminum, to an interface, it is a metal layer. It seems that adhesion with a M-Cr-aluminum-Y alloy layer is not reduced. Therefore, the exfoliation from a diffusion barrier layer interface etc. can be prevented effectively.

[0014] Even if it uses a heat-resistant member by these under conditions which are exposed to long duration hot environments, it is the fall of the high temperature strength of a base material by the above-mentioned diffusion barrier layer. Since the exfoliation accompanying having made the diffusion barrier layer intervene etc. can be prevented while being able to prevent the anticorrosion of a M-Cr-aluminum-Y alloy layer, an oxidation-resistant fall, etc., it becomes possible to use a heat-resistant member for stability for a long period of time.

[0015] Moreover, according to the manufacture approach of the heat-resistant member of this invention, the 1st heat-resistant member mentioned above is stabilized, and it can produce with sufficient repeatability.

[0016] It is as being chosen as a diffusion barrier layer out of nickel, Co, and Fe in the 2nd heat-resistant member of this invention that it is few. To the inside of the matrix phase which uses one sort of elements as a principal component $Ma1(A1-x Bx)$ -a The ingredient with which the phase deposited is used. Since migration length of an element can be lengthened according to the diffusion suppression effectiveness in the interface of a matrix phase and a sludge phase ($Ma1(A1-x Bx)$ -a phase), this diffusion barrier layer is a base material. It becomes possible to control the element migration between M-Cr-aluminum-Y alloy layers. Moreover, since it has the metal matrix phase, a diffusion barrier layer is a base material. The adhesion which was excellent to the M-Cr-aluminum-Y alloy layer is shown. Therefore, even if it uses a heat-resistant member under conditions which are exposed to long duration hot environments, it is the fall of the high temperature strength of a base material. Since the exfoliation accompanying having made the diffusion barrier layer intervene etc. can be prevented while being able to prevent the anticorrosion of a M-Cr-aluminum-Y alloy layer, an oxidation-resistant fall, etc., it becomes possible to use a heat-resistant member for stability for a long period of time.

[0017]

[Embodiment of the Invention] Hereafter, the gestalt for carrying out this invention is explained.

[0018] Drawing 1 is the sectional view showing the operation gestalt of the 1st heat-resistant member of this invention. in this drawing, 1 is a metal base and is chosen from nickel, Co, and Fe as this metal base 1 -- at least -- the heat-resistant alloy used as a principal component uses one sort of elements -- having -- a use application etc. -- responding -- various kinds -- a well-known heat-resistant alloy can be used, choosing it suitably. Practically, it is effective to use Co radical superalloy of nickel radical superalloy of IN738, IN738LC, IN939, Mar-M247, RENE80, CM-247, CMSX-2, and CMSX-4 grade, FSX-414, and Mar-M509 grade.

[0019] On the above-mentioned metal base 1, the metal layer 2 which functions as a diffusion barrier layer is formed, and this metal layer 2 is minded. Covering formation of the M-Cr-aluminum-Y alloy layer 3 is carried out as anticorrosion and an anti-oxidation metal coating layer. The heat-resistant member 4 is constituted by these.

[0020] The metal layer 2 formed as a diffusion barrier layer Ti, Zr, Hf, V, It is as being chosen out of Ta and Nb that it is few. One sort of metals, or Ti, it is chosen out of Zr, Hf, and V, Ta and Nb -- at

least -- it is chosen out of one sort of elements, and nickel, Co and Fe -- at least -- an alloy with one sort of elements is used as a principal component, and it is chosen as these out of oxygen and nitrogen -- at least -- It consists of a layer in which one sort dissolved.

[0021] Here, many alloys of these, nickel, Co, Fe, etc., etc. can dissolve oxygen and nitrogen.

[metals, such as Ti, Zr, Hf, and V Ta, Nb,] The metal layer 2 which dissolve such oxygen and nitrogen is with the metal base 1 since the diffusion coefficient of elements, such as aluminum, is small. It functions as a diffusion barrier layer with the M-Cr-aluminum-Y alloy layer 3.

[0022] Thus, although metal layer 2 the very thing which dissolved mostly also functions as a diffusion barrier layer, oxygen and nitrogen Even if it heat-treats after metal layer 2 membrane formation or does not heat-treat, when the metal layer 2 receives heat at the time of real use Oxygen or nitrogen which dissolves in the above-mentioned metal layer 2 As aluminum in the M-Cr-aluminum-Y alloy layer 3 etc. reacts and it is shown in drawing 2 , it is with the metal layer 2 like. An oxide or nitrides (aluminum $2O_3$, AlN) 5, such as aluminum, generate to an interface with the M-Cr-aluminum-Y alloy layer 3. These aluminum $2O_3$ That is [matter, such as AlN (5), has the small diffusion coefficient of the element in the matter and it can use effectively as a diffusion barrier layer], many metal layers 2 which consist of a metal mentioned above or an alloy can dissolve oxygen and nitrogen. - It excelled in a way, and anticorrosion and oxidation resistance. The activity of aluminum element in an alloy is high to - **, and a M-Cr-aluminum-Y alloy is in aluminum $2O_3$ and a nitriding ambient atmosphere in an oxidizing atmosphere. It is easy to generate AlN. Therefore, metal layer 2 which dissolve oxygen and nitrogen If the heat at the time of heat treatment or real use is received after the M-Cr-aluminum-Y alloy layer 3 has touched, they are the oxygen in the metal layer 2, or nitrogen. aluminum in the M-Cr-aluminum-Y alloy layer 3 etc. reacts, and an oxide or nitrides 5, such as aluminum, generate to an interface.

[0023] Oxide or nitrides 5, such as these aluminum, are with a metal base 1, even if the diffusion coefficient in the interior is small, and it uses the heat-resistant member 4 under conditions which are exposed to hot environments for a long time, since it functions effectively as a diffusion barrier layer. The element migration between the M-Cr-aluminum-Y alloy layers 3 can be controlled. As the result, it is the fall of the high temperature strength of a metal base 1. The anticorrosion of the M-Cr-aluminum-Y alloy layer 3, an oxidation-resistant fall, etc. can be prevented, and it becomes possible to use the heat-resistant member 4 for stability for a long period of time.

[0024] And the diffusion barrier layer of the former [layer / 2 (oxide or nitrides 5, such as aluminum, are included) / which functions as a diffusion barrier layer mentioned above / metal], namely, aluminum $2O_3$ etc. -- from -- a greatly different point from what formed the becoming ceramic layer directly The metal layer 2 which functions as a diffusion barrier layer is a layer (metallic layer) which essentially has metallic physical properties, and in a metal base 1, it shows very good adhesion in order to form a metal/metallic bond. Moreover, metal layer 2 Even if it forms an oxide or nitrides 5, such as aluminum, in an interface with the M-Cr-aluminum-Y alloy layer 3, these are with the metal layer 2. Since it is a resultant in an interface with the M-Cr-aluminum-Y alloy layer 3, it is with the metal layer 2. It seems that it acts in the direction which raises the integrated state of the M-Cr-aluminum-Y alloy layer 3, and adhesion is not reduced. Therefore, the exfoliation from an interface with a diffusion barrier layer etc. can be prevented so that existence of a diffusion barrier layer cannot reduce the adhesion between each class of the heat-resistant member 4. The reinforcement of the heat-resistant member 4 is attained by this.

[0025] Although especially the oxygen content or nitrogen content in the metal layer 2 which dissolves the oxygen mentioned above and nitrogen is not limited, it must be the oxygen content or nitrogen content to which metal layer 2 the very thing can maintain metallic physical properties at least. Although it changes also with configuration elements of the metal layer 2 from such a point, it is the oxygen content or nitrogen content of the metal layer 2. It is desirable that it is less than [40at%]. The amount of oxygen or nitrogen volume in the metal layer 2 When 40at% is exceeded, an oxide and a nitride generate in the metal layer 2, and there is a possibility that the metallic property of metal layer 2 original may fall. Moreover, metal layer 2 An oxide or nitrides 5, such as superfluous aluminum, generate to an interface with the M-Cr-aluminum-Y alloy layer 3, and there is a possibility that interfacial peeling etc. may arise. On the other hand, if there is not much little the amount of oxygen or nitrogen volume in the metal layer 2, while the function as a diffusion barrier

layer of metal layer 2 the very thing will fall, the amount of generation of oxides, such as aluminum in an interface, or a nitride 5 becomes inadequate. As for the oxygen content or nitrogen content of the metal layer 2, from such a point, it is desirable that it is more than 5at%.

[0026] Moreover, especially the thickness of the metal layer 2 which dissolves oxygen and nitrogen is because of acquiring the good diffusion barrier effectiveness to stability, although not limited. 5 micrometers It is 50 micrometers, when considering as the above is desirable and it prevents exfoliation of metal layer 2 the very thing etc. Considering as the following is desirable.

[0027] The metal layer 2 is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb as it is few. It is as being chosen as one sort of metal layers out of oxygen and nitrogen that it is few. Although the function as a fundamental diffusion barrier layer can be obtained as mentioned above by making one sort dissolve While controlling the element migration from a metal base 1 side, in order to raise adhesion with a metal base 1 etc. It is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb that it is few. It is as being chosen out of one sort of elements, and nickel, Co and Fe that it is few. It is desirable to consider as an alloy layer with one sort of elements. The content of these nickel, Co, and Fe is 50at(s)% so that it may not have a bad influence on the amount of dissolution of the oxygen in the metal layer 2, or nitrogen. Considering as the following is desirable. Moreover, it is 10at(s)%, in order to be stabilized and to control the element migration from a metal base 1 side. It is desirable to make it contain above.

[0028] The dissolving metal layer 2 is the following, and can make and form oxygen which was mentioned above, and nitrogen.

[0029] That is, it is as being chosen as the front face of a metal base 1 out of Ti, Zr, Hf, and V, Ta and Nb that it is few. Oxygen tension or a nitrogen partial pressure the metal layer containing one sort of elements Membranes are formed in the ambient atmosphere of 0.1 - 1×10^4 Pa. Here, as the membrane formation approach, plasma metal spray methods, such as low pressure plasma spraying, epsilonB-PVD, the magnetron sputtering method, a CVD method, etc. are applicable.

[0030] Here, a plasma metal spray method has a quick membrane formation rate, and it excels as an approach of forming a thick film. Since especially a low-pressure-plasma-spraying method can control superfluous oxidation reaction etc. while being able to form a precise layer, it is often used for membrane formation of a metal layer. For example, while applying such a low-pressure-plasma-spraying method, it is the oxygen tension or nitrogen partial pressure in a thermal-spraying ambient atmosphere. As range of 0.1 - 1×10^4 Pa It is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb that it is few. One sort of simple substance metal layers, Or it is as being chosen out of Ti, Zr, Hf, and V, Ta and Nb that it is few. It is as being chosen out of one sort of elements, and nickel, Co and Fe that it is few. If an alloy layer with one sort of elements is formed The metal layer 2 in which oxygen and nitrogen which exist in an ambient atmosphere in a thermal-spraying process at a minute amount dissolve in a simple substance metal layer or an alloy layer, and dissolve oxygen and nitrogen can be obtained. In addition, it is the same when applying the method of forming membranes other than a plasma metal spray method.

[0031] The oxygen tension or nitrogen partial pressure at the time of metal layer 2 formation Oxygen or nitrogen cannot be made to fully dissolve that it is less than 0.1Pa in the metal layer 2, but there is a possibility that the diffusion barrier effectiveness mentioned above may fall, and it is one side. If 1×10^4 Pa is exceeded, oxidation and nitriding of metal layer 2 the very thing will take place, the metallic physical properties of the metal layer 2 deteriorate, and the adhesion of the metal layer 2 falls.

[0032] The formation approach of the metal layer 2 which dissolves oxygen and nitrogen can form the metal layer 2 which dissolves oxygen or nitrogen which was mentioned above also by using the matter which carries out optimum dose content of oxygen or the nitrogen for the oxygen mentioned above or nitrogen not only at membrane formation in a minute amount **** ambient atmosphere but at a membrane formation raw material.

[0033] M-Cr-aluminum-Y alloy layer 3 after forming the metal layer 2 which dissolves oxygen and nitrogen by approach which was described above Membranes are formed in the reduced pressure ambient atmosphere below 1×10^4 Pa. this -- A low-pressure-plasma-spraying method, epsilonB-PVD, the magnetron sputtering method, a CVD method, etc. are applicable also to formation of the M-Cr-aluminum-Y alloy layer 3. The ambient atmosphere at the time of forming the M-Cr-

aluminum-Y alloy layer 3 If 1×10^4 Pa is exceeded, the adhesion of a cause and the M-Cr-aluminum-Y alloy layer 3 will fall [oxidation etc.] on metal layer 2 front face at the time of membrane formation. after [moreover,] forming the M-Cr-aluminum-Y alloy layer 3 -- this -- In forming an oxide or nitrides 5, such as aluminum, in the interface of the M-Cr-aluminum-Y alloy layer 3 and the metal layer 2 beforehand, it heat-treats at about 1000- 1500K temperature in the inert atmosphere of nitrogen, an argon, etc., and a reduced pressure ambient atmosphere.

[0034] it mentioned above when the M-Cr-aluminum-Y alloy layer 3 obtains a function as the anticorrosion and oxidation-resistant coating of a metal base 1 -- general -- 0.1 - 20 % of the weight aluminum and 10 - 35 % of the weight Cr and 0.1 - 5 % of the weight the remainder is chosen from nickel, Co, and Fe including Y -- at least -- The alloy of the presentation which becomes substantial is used from one sort of M elements. moreover, application a M-Cr-aluminum-Y alloy -- Ti, Nb, Hf, Zr, and Ta -- and -- it is chosen out of W -- at least -- One sort of alloying elements 5 % of the weight It is also possible to carry out minute amount addition in the following range.

[0035] The metal layer 2 which dissolves oxygen and nitrogen in metal base 1 front face is minded. Although the member 4 covered with the M-Cr-aluminum-Y alloy layer 3 may be used as a heat-resistant member as it is, as shown in drawing 3 depending on a use application Further On the M-Cr-aluminum-Y alloy layer 3, by using the ceramic layer 6 as a thermal-barrier-coating layer, covering formation can be carried out and the member 7 of such a configuration can also be used as a heat-resistant member.

[0036] Although various ceramic ingredients, such as Si_3N_4 , SiC, aluminum 2O_3 , ZrO_2 , TiN, AlN, and sialon, can be used for the above-mentioned ceramic layer 6, it is from the lowness of thermal conductivity, the magnitude of a coefficient of thermal expansion, etc. ZrO_2 It is suitable. moreover, ZrO_2 As the stabilizing agent which inhibits a phase transformation Y_2O_3 most -- desirable -- especially -- Y_2O_3 Partial stabilization included about 8% of the weight ZrO_2 The property which was most excellent synthetically is shown. In addition, the ceramic layer 6 is aluminum 2O_3 formed by performing aluminum-ized processing of the aluminum packing method etc. You may be a layer etc.

[0037] Next, the operation gestalt of the 2nd heat-resistant member of this invention is described with reference to drawing 4 and drawing 5 . Drawing 4 is the sectional view showing 1 operation gestalt of the 2nd heat-resistant member of this invention, and 11 is a metal base which consists of the same ingredient as the operation gestalt mentioned above. It is the same as that of the operation gestalt which the diffusion barrier layer 12 is formed on this metal base 11, and was mentioned above through this diffusion barrier layer 12. Covering formation of the M-Cr-aluminum-Y alloy layer 13 is carried out. The heat-resistant member 14 is constituted by these.

[0038] The above-mentioned diffusion barrier layer 12 is as being chosen out of nickel, Co, and Fe as it is few. In the matrix phase used as a principal component, one sort of elements $\text{Ma}_1(\text{A}_{1-x}\text{B}_x)\text{-a}$ phase (as being chosen out of nickel, Co, and Fe, M a 1 sort element as it is few) A is as being chosen out of aluminum, Ti, Nb, and Ta as it is few. One sort of elements B -- Cr, Mo, and W, Hf and Re -- and -- it is chosen out of Y -- at least -- one sort of elements are shown -- a -- and -- $x \cdot 0.3 \leq a \leq 0.8$ and $0 \leq x < 0.5$ -- it is -- it consists of a depositing ingredient.

[0039] Unlike the conventional diffusion barrier layer, this diffusion barrier layer 12 is with a metal base 11 by lengthening migration length of an element according to the diffusion suppression effectiveness in the interface of a matrix phase and a deposit phase ($\text{Ma}_1(\text{A}_{1-x}\text{B}_x)\text{-a}$ phase). The element migration between the M-Cr-aluminum-Y alloy layers 13 is controlled. $\text{Ma}_1(\text{A}_{1-x}\text{B}_x)\text{-a}$ Phase the value of a -- the above -- a stable deposit phase is not obtained as it is out of range. It is with a metal base 11 about such a diffusion barrier layer 12. Even if it uses the heat-resistant member 14 under conditions which are exposed to hot environments for a long time by making it intervene between the M-Cr-aluminum-Y alloy layers 13, the element migration between a metal base 11 and the M-Cr-aluminum-Y alloy layer 13 can be controlled. Therefore, the fall of the high temperature strength of a metal base 11, the anticorrosion of the M-Cr-aluminum-Y alloy layer 13, an oxidation-resistant fall, etc. can be prevented, and reinforcement of the heat-resistant member 14 can be attained.

[0040] $\text{Ma}_1(\text{A}_{1-x}\text{B}_x)\text{-a}$ in the diffusion barrier layer 12 in order to acquire the diffusion barrier effectiveness which was mentioned above It is needed that there are more amounts of deposits of a

phase (rate of the volume) than the rate of the volume of the deposit phase in a metal base 11. Because, since the path of the element which diffuses the inside of a matrix phase becomes short and it becomes impossible to have an one or more-metal base diffused resistor when the rate of the volume of the deposit phase in the diffusion barrier layer 12 is lower than it in a metal base 11, it is because the function as a diffusion barrier layer 12 is not obtained. Usually, when a metal base 11 consists of a nickel radical alloy, for example, the sludge of the nickel3 aluminum equality of 50 - 60 volume % is included, it thinks from this, and, as for the diffusion barrier layer 12, it is desirable that the deposit phase more than 50 volume % is included. Moreover, if the rate of the volume is close to 100%, in order that a brittleness-mechanical property peculiar to an intermetallic-compound phase may actualize, it is the rate of the volume of a deposit phase. Considering as 90% or less is desirable.

[0041] And since the diffusion barrier layer 12 mentioned above makes the metal phase the matrix, it does not have brittleness [like the diffusion barrier layer which forms a metal/metallic bond, and shows very good adhesion, and consists of monolayers, such as conventional oxide, a nitride, and an acid nitride,] whose metal base 1 is, either. Therefore, since the exfoliation accompanying having made the diffusion barrier layer 12 intervene etc. can be prevented in addition to the diffusion barrier effectiveness mentioned above, it becomes possible to use the heat-resistant member 14 for stability for a long period of time.

[0042] As a matrix phase of the diffusion barrier layer 12 It is as being chosen out of nickel, Co, and Fe that it is few. One sort of elements are used as a principal component. It generates to this. $Ma1(A1-x Bx)$ -a The element according to a phase, that is, it is chosen out of aluminum, Ti, Nb, and Ta - - at least -- one sort of elements, and the need -- responding -- Cr, Mo, and W, Hf and Re -- and -- it is chosen out of Y -- at least -- The solid solution to which one sort of elements dissolved is used. According to the amount of these dissolution element, and the amount of deposits of a $Ma1(A1-x Bx)$ -a phase, it is set up suitably. Thus, the matrix phase of the diffusion barrier layer 12 is as being chosen out of nickel, Co, and Fe as it is few. Although what is necessary is just the solid solution which uses one sort of elements as a principal component, it is desirable to use nickel as a principal component, if a metal base 1 is nickel radical alloy, and to use Co as a principal component from a viewpoint which prevents generation of adjustment with a metal base 1 and the different-species phase in a metal base 1, if it is Co radical alloy.

[0043] Moreover, a deposit phase is as being chosen out of nickel, Co, and Fe as it is few. One sort of elements (M element), and aluminum, It is as being chosen out of Ti, Nb, and Ta that it is few. Be [what is necessary / just although one sort of elements (A element) are included by the predetermined ratio] In using the matrix phase which uses nickel as a principal component, for example, nickel0.75 (aluminum, Ti, Nb) 0.25 (nickel3 (aluminum, Ti, Nb)), Intermetallic-compound phases, such as nickel0.5 aluminum0.5 (NiAl) and nickel0.25aluminum0.75 (NiAl3), Moreover, when using the matrix phase which uses Co as a principal component, the intermetallic-compound (CoAl) phase of Co0.5 aluminum0.5 etc. is desirable from points, such as thermal and chemical stability. in order [moreover,] to raise the stability of a deposit phase, or to disturb adjustment with a matrix phase and to raise the resistance over element diffusion -- Cr, Mo, and W, Hf and Re -- and -- it is chosen out of Y -- at least -- One sort of elements (B element) can permute some A elements. However, B yuan quantum It is made not to exceed the quantum of A yuan.

[0044] by the way, the M-Cr-aluminum-Y alloy layer 13 -- general -- a parent phase like [when M element is nickel] a NiAl phase -- moreover -- Also when M element is Co, a parent phase like a CoAl phase is mainly included. Therefore, when the deposit phase in the diffusion barrier layer 12 is a parent phase, it is the rate of the volume. It is more desirable than the rate of the volume in the M-Cr-aluminum-Y alloy layer 13 to make [many] it. By this, migration of aluminum from the M-Cr-aluminum-Y alloy layer 13 etc. can be controlled much more effectively. On the other hand, since the metal base 1 mainly contains gamma' phase of nickel3 aluminum equality, it is also effective to make the deposit phase in the diffusion barrier layer 12 into gamma' phase. That is, migration of aluminum from the M-Cr-aluminum-Y alloy layer 13 etc. can be effectively controlled by bringing the sludge presentation of the diffusion barrier layer 12 close to a metal base 11.

[0045] Although especially the thickness of the diffusion barrier layer 12 mentioned above is not limited, in order that it may acquire the good diffusion barrier effectiveness to stability 1 micrometer

When considering as the above is desirable and it prevents exfoliation of diffusion barrier layer 12 the very thing etc. 200 micrometers Considering as the following is desirable. moreover -- the formation approach of the diffusion barrier layer 12 -- a plasma metal spray method and HVOF -- various membrane formation processes, such as law, PVD, and a CVD method, are applicable, and since a membrane formation rate and the width of face of ingredient selection are especially wide, a plasma metal spray method is effective. While the low-pressure-plasma-spraying method (vapor phase soldering) for performing a thermal-spraying process in a reduced pressure ambient atmosphere is desirable and being able to control the oxidation at the time of a process by this also in a plasma metal spray method, a precise enveloping layer can be formed. The same is said of the formation approach of the M-Cr-aluminum-Y alloy layer 13. The diffusion barrier layer 12 is minded for metal base 11 front face. Like [although the member 14 covered with the M-Cr-aluminum-Y alloy layer 13 may be used as a heat-resistant member as it is] the operation gestalt mentioned above, as shown in drawing 5 depending on a use application Further On the M-Cr-aluminum-Y alloy layer 13, by using the ceramic layer 15 as a thermal-barrier-coating layer, covering formation can be carried out and the member 16 of such a configuration can also be used as a heat-resistant member. As for the configuration of the ceramic layer 15, it is desirable to suppose that it is the same as that of the operation gestalt mentioned above.

[0046]

[Example] Next, the concrete example of this invention is explained.

[0047] To the front face of the round bar ingredient which consists of example 1 nickel radical superalloy CM-247, it is abbreviation. It is 10 micrometers in thickness by the low-pressure-plasma-spraying method in 100Pa reduced pressure atmospheric air. Ti layer was formed. The oxygen tension in the thermal-spraying ambient atmosphere in this case is about 25Pa. Subsequently, it is thickness within the same chamber. 150 micrometers The NiCoCrAlY layer (nickel-23%Co-17%Cr-12%aluminum-0.5%Y (% of the weight)) was formed. place which measured the amount of oxygen in the above-mentioned Ti layer 33at% -- it was.

[0048] Thus, it is all over Ar ambient atmosphere furnace to the obtained heat-resistant member. Heat treatment of 1000 hours was performed by 1273K. When the creep test was performed in the sample after this heat treatment under the stress of 250MPa(s) by 1173K, fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, they are Ti layer from a base material side, and aluminum 2O3. It existed in order of the layer and the NiCoCrAlY layer.

[0049] Moreover, it is this presentation directly by the low-pressure-plasma-spraying method as an example of a comparison with this invention to the front face of the round bar ingredient which consists of nickel radical superalloy CM-247. In the sample which formed the NiCoCrAlY layer, it heat-treated on the same conditions as the above-mentioned example 1. It fractured, when the creep test of the sample after this heat treatment was performed under the same conditions, and 80 hours passed. When this sample was cut and cross-section observation was performed, within the base material near the interface, disappearance of a strengthening phase (gamma' phase) was accepted and the brittle generation phase which consists of Cr-W further was observed.

[0050] example 2 nickel radical superalloy IN738 from -- the front face of the becoming round bar ingredient -- the inside of about 10Pa reduced pressure atmospheric air -- a low-pressure-plasma-spraying method -- 15 micrometers in thickness The Ti-50at%nickel layer was formed. The oxygen tension in the thermal-spraying ambient atmosphere in this case is abbreviation. It is 2Pa. Subsequently, it is thickness within the same chamber. 100 micrometers CoNiCrAlY The layer (Co-32%nickel-21%Cr-8%aluminum-0.5%Y (% of the weight)) was formed. the above-mentioned Ti-50at% -- place which measured the amount of oxygen in nickel layer 15at% -- it was.

[0051] Thus, 1123K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 300MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, it is from a base material side. A Ti-nickel-O layer and aluminum 2O3 It existed in order of the layer and the CoNiCrAlY layer.

[0052] moreover -- as the example of a comparison with this invention -- nickel radical superalloy IN738 from -- the front face of the becoming round bar ingredient -- a low-pressure-plasma-spraying

method -- direct -- this presentation In the sample which formed the CoNiCrAlY layer, it heat-treated on the same conditions as the above-mentioned example 2. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 60-hour progress. When this sample was cut and cross-section observation was performed, within the base material near the interface, disappearance of a strengthening phase (gamma' phase) was accepted and the brittle generation phase which consists of Cr-W further was observed.

[0053] To the front face of the round bar ingredient which consists of example 3 nickel radical superalloy CM-247, it is 15 micrometers in thickness by the low-pressure-plasma-spraying method in about 1000Pa reduced pressure atmospheric air. The Ta-50at%nickel layer was formed. The oxygen tension in the thermal-spraying ambient atmosphere in this case is abbreviation. It is 200Pa. Subsequently, it is thickness within the same chamber. 120 micrometers The CoNiCrAlY layer (an example 2 and this presentation) was formed. the above-mentioned Ta-50at% -- place which measured the amount of oxygen in nickel layer 10at% -- it was.

[0054] Thus, 1173K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 250MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, it is from a base material side. A Ta-nickel layer and aluminum 2O3 It existed in order of the layer and the CoNiCrAlY layer.

[0055] Moreover, it is this presentation directly by the low-pressure-plasma-spraying method as an example of a comparison with this invention to the front face of the round bar ingredient which consists of nickel radical superalloy CM-247. In the sample which formed the CoNiCrAlY layer, it heat-treated on the same conditions as the above-mentioned example 3. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 85-hour progress. When this sample was cut and cross-section observation was performed, disappearance of a strengthening phase (gamma' phase) was accepted within the base material near the interface.

[0056] example 4Co radical superalloy FSX-414 from -- the front face of the becoming round bar ingredient -- the inside of about 50Pa reduced pressure atmospheric air -- a low-pressure-plasma-spraying method -- 15 micrometers in thickness The Nb-50at%Co layer was formed. The oxygen tension in the thermal-spraying ambient atmosphere in this case is abbreviation. It is 5Pa. Subsequently, it is thickness within the same chamber. 100 micrometers CoNiCrAlY The layer (an example 2 and this presentation) was formed. the above-mentioned Nb-50at% -- the place which measured the amount of oxygen in Co layer -- 5at% -- it was.

[0057] Thus, 1023K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 200MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, it is from a base material side. Nb-Co layer, aluminum2 O3 It existed in order of the layer and the CoNiCrAlY layer.

[0058] moreover -- as the example of a comparison with this invention -- Co radical superalloy FSX-414 from -- the front face of the becoming round bar ingredient -- a low-pressure-plasma-spraying method -- direct -- this presentation In the sample which formed the CoNiCrAlY layer, it heat-treated on the same conditions as the above-mentioned example 4. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 50-hour progress. When this sample was cut and cross-section observation was performed, disappearance of a strengthening phase (gamma' phase) was accepted within the base material near the interface.

[0059] To the front face of the round bar ingredient which consists of example 5nickel radical superalloy CM-247, it is abbreviation. It is thickness by EB-PVD in a 1Pa oxygen ambient atmosphere. 5 micrometers The Zr-Nb layer was formed. Subsequently, it is thickness within the same chamber. 130 micrometers The NiCoCrAlY layer (an example 1 and this presentation) was formed, and the metallic-coating layer was formed. Furthermore on it, it is EB-PVD. Y2 O 3 Stabilization ZrO2 Layer 200 micrometers It formed by thickness. Above Place which measured the amount of oxygen in a Zr-Nb layer It was 20at%.

[0060] Thus, 1173K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 250MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation

was performed, it is from a base material side. Zr-Nb layer, aluminum₂O₃ It existed in order of the layer and the NiCoCrAlY layer.

[0061] Moreover, it is this presentation directly by EB-PVD as an example of a comparison with this invention to the front face of the round bar ingredient which consists of nickel radical superalloy CM-247. A NiCoCrAlY layer is formed and it is on it further. Y₂O₃ Stabilization ZrO₂ In the sample in which the layer was formed, it heat-treated on the same conditions as the above-mentioned example 5. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 90-hour progress. When this sample was cut and cross-section observation was performed, within the base material near the interface, disappearance of a strengthening phase (gamma' phase) was accepted and the brittle generation phase which consists of Cr-W further was observed.

[0062] To the front face of the round bar ingredient which consists of example 6 nickel radical superalloy CM-247, it is abbreviation. It is thickness by EB-PVD in a 1Pa oxygen ambient atmosphere. 8 micrometers The Ti-Nb layer was formed. Subsequently, it is 80 micrometers in thickness within the same chamber. The NiCoCrAlY layer (an example 1 and this presentation) was formed, and the metallic-coating layer was formed. Furthermore on it, it is EB-PVD. Y₂O₃ Stabilization ZrO₂ Layer 250 micrometers It formed by thickness. Above Place which measured the amount of oxygen in a Ti-Nb layer It was 10at%.

[0063] Thus, 1173K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 250MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, it is from a base material side. It existed in order of the Ti-Nb-O layer and the NiCoCrAlY layer.

[0064] Moreover, it is this presentation directly by EB-PVD as an example of a comparison with this invention to the front face of the round bar ingredient which consists of nickel radical superalloy CM-247. A NiCoCrAlY layer is formed and it is on it further. Y₂O₃ Stabilization ZrO₂ In the sample in which the layer was formed, it heat-treated on the same conditions as the above-mentioned example 6. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 90-hour progress. When this sample was cut and cross-section observation was performed, within the base material near the interface, disappearance of a strengthening phase (gamma' phase) was accepted and the brittle generation phase which consists of Cr-W further was observed.

[0065] To the front face of the round bar ingredient which consists of example 7 nickel radical superalloy CM-247, it is 20 micrometers in thickness by the low-pressure-plasma-spraying method in about 10Pa reduced pressure atmospheric air. The Nb-30at%nickel layer was formed. The oxygen tension in the thermal-spraying ambient atmosphere in this case is abbreviation. It is 4Pa. Subsequently, it is thickness within the same chamber. 100 micrometers NiCoCrAlY The layer (an example 1 and this presentation) was formed. the above-mentioned Nb-30at% -- the place which measured the amount of oxygen in nickel layer -- 5at% -- it was.

[0066] Thus, 1123K after heat-treating on the same conditions as an example 1 to the obtained heat-resistant member When the creep test was performed under the stress of 300MPa(s), fracture was not seen even if held for 100 hours. Moreover, when this sample was cut and cross-section observation was performed, it is from a base material side. A Nb-nickel-O layer and aluminum₂O₃ It existed in order of the layer and the NiCoCrAlY layer.

[0067] Moreover, it is thickness by EB-PVD as an example of a comparison with this invention to the front face of the round bar ingredient which consists of nickel radical superalloy CM-247. 2 micrometers aluminum₂O₃ A layer is formed and they are an example 7 and this presentation further. In the sample which formed the NiCoCrAlY layer, it heat-treated on the same conditions as the above-mentioned example 7. When the creep test of the sample after this heat treatment was performed under the same conditions, it fractured after 80-hour progress. When this sample was cut and cross-section observation was performed, it is aluminum₂O₃. The interface and aluminum₂O₃ of a layer and a base material Layer It turned out that exfoliation has arisen from the interface with a NiCoCrAlY layer, and this exfoliation causes fracture.

[0068] example 8 nickel radical superalloy IN738 from -- the becoming base material -- the

dimension of 20x20x3 mm -- processing it -- the front face -- a nickel-10%Co-17%aluminum alloy (% of the weight) -- as a thermal-spraying raw material -- using -- a low-pressure-plasma-spraying method -- 50 micrometers in thickness The diffusion barrier layer was formed. Subsequently, it is thickness on this diffusion barrier layer. 150 micrometers Covering formation of the NiCoCrAlY layer (nickel-23%Co-17%Cr-12%aluminum-0.5%Y (% of the weight)) was carried out by the low-pressure-plasma-spraying method. The above-mentioned diffusion barrier layer is a rate of the volume. It had 71% of nickel3 aluminum phase. Moreover, rate of the volume of the nickel3 aluminum phase in a base material It was 52%.

[0069] moreover, nickel radical superalloy IN738 into which the above-mentioned example 8 and this dimension were processed as an example of a comparison with this invention from -- the becoming base material front face -- the above-mentioned example 8 and this presentation a NiCoCrAlY layer -- thickness 200 micrometers Direct covering formation was carried out.

[0070] Each of these samples It was exposed to the oxidation test in atmospheric air of 1173Kx 5000h. As a result of observing the cross section of each sample by SEM after a trial, at the sample of the example of a comparison, it is 36 micrometers from a front face. At the sample by the example 8 although the oxide layer was growing by thickness, it is 13 micrometers. It was extent. Moreover, when gazed at the organization of a NiCoCrAlY layer, it was the configuration that the NiAl phase deposited in the matrix phase which all uses nickel as a principal component in an initial state with sufficient aluminum concentration, but after heat treatment, by the sample of the example of a comparison, as a result of spreading aluminum in a base material side by heat treatment, the NiAl phase had disappeared completely. - Although aluminum was consumed by generation of an oxide near the front face of a NiCoCrAlY layer by the sample of a way and an example 8 and the NiAl phase had disappeared, it is 23 micrometers from a front face. It turned out like the first stage that it consists of nickel and a NiAl phase and the above interior has diffusion depressor effect with the sufficient diffusion barrier layer by this invention. furthermore, the place which measured the thickness of the different-species phase in a base material -- sample of the example of a comparison 127 micrometers it was -- a thing -- receiving -- the sample of an example 8 -- 23 micrometers It turned out that it has become and the diffusion barrier layer by this invention contributes also to suppression of a fall of a base material on the strength effectively.

[0071] example 9nickel radical superalloy IN738 from -- the becoming base material -- the dimension of 20x20x3 mm -- processing it -- the front face -- a nickel-10%Co-17%aluminum alloy (% of the weight) -- as a thermal-spraying raw material -- using -- a low-pressure-plasma-spraying method -- 20 micrometers in thickness The diffusion barrier layer was formed. Subsequently, it is thickness on this diffusion barrier layer. 100 micrometers Covering formation of the NiCoCrAlY layer (an example 8 and this presentation) was carried out by the low-pressure-plasma-spraying method. Furthermore, it is on the maximum front face. ZrO₂-8wt%Y₂O₃ 200 micrometers Covering formation was carried out. Rate of the volume of the nickel3aluminum phase in a base material It is 55% and is the rate of the volume of the nickel3 aluminum phase of a diffusion barrier layer. It was 74%. moreover, nickel radical superalloy IN738 into which the above-mentioned example 9 and this dimension were processed as an example of a comparison with this invention from -- the becoming base material front face -- the above-mentioned example 9 and this presentation a NiCoCrAlY layer -- thickness 100 micrometers direct covering formation -- carrying out -- further -- the maximum front face ZrO₂-8wt%Y₂O₃ 200 micrometers Covering formation was carried out.

[0072] These samples It was exposed to the oxidation test in atmospheric air of 1173Kx 5000h. As a result of observing the cross section of each sample by SEMu after a trial, it is at the sample of the example of a comparison. It is 28 micrometers from an interface with a ceramic layer to the interior of a NiCoCrAlY layer. Although the oxide layer was growing by thickness, it is at the sample of an example 9. 9 micrometers It was extent. Moreover, when gazed at the organization of a NiCoCrAlY layer, it was the configuration that the NiAl phase deposited in the matrix phase which all uses nickel as a principal component in an initial state with sufficient aluminum concentration, but after heat treatment, by the sample of the example of a comparison, as a result of spreading aluminum in a base material, the NiAl phase had disappeared completely. - Although aluminum was consumed by generation of an oxide near the interface of a ceramic layer / NiCoCrAlY layer and the NiAl phase

had disappeared by the sample of a way and an example 9, it is 13 micrometers from an interface. It turned out that it consists of nickel and a NiAl phase like the first stage inside above, and has diffusion depressor effect with the sufficient diffusion barrier layer of this invention. furthermore, the place which measured the thickness of the different-species phase in a base material -- example of a comparison 108 micrometers it was -- although -- an example 9 -- 16 micrometers It turned out that it has become and the diffusion barrier layer of this invention contributes also to suppression of a fall of a base material on the strength effectively.

[0073] The base material which consists of example 10 single-crystal nickel radical superalloy CMSX-2 is processed into the dimension of 20x20x3 mm, a nickel-15%aluminum-17%Cr alloy (% of the weight) is used for the front face as a thermal-spraying raw material, and it is 20 micrometers in thickness with a low-pressure-plasma-spraying method. The diffusion barrier layer was formed. Subsequently, it is 80 micrometers in thickness about a CoNiCrAlY layer (Co-32%nickel-21%Cr-8%aluminum-0.5%Y (% of the weight)). Covering formation was carried out. In this sample 1323Kx16h+1123Kx48h It heat-treated. Although the parent phase (NiAl phase) deposited by making gamma phase (nickel solid solution) into a matrix also with each enveloping layer as a result of SEmu observation of a cross section, it is the rate of the volume of this parent phase. In a CoNiCrAlY layer, it is at 44% and a diffusion barrier layer. It was 69%. Moreover, it consists of a gamma phase and a gamma' phase (nickel3 aluminum phase), and a base material is the rate of the volume of gamma' phase. It was 52%.

[0074] Moreover, the sample was produced in the same process as an example of a comparison with this invention except not forming a nickel-aluminum-Cr layer in the middle. The phase configuration in each part of this sample and a CoNiCrAlY layer are a rate of the volume in gamma phase matrix. Having 46% of parent phase, a base material is a rate of the volume in gamma phase. It had 56% of gamma' phase.

[0075] Each [these] sample 1173Kx5000h The oxidation test in quiescence atmospheric air was presented. As a result of performing cross-section observation of each sample after a trial, by the sample of the example of a comparison, a parent phase disappears completely from an enveloping layer, and a scaling layer is also 37 micrometers from a front face. It was growing up to thickness. on the other hand -- the sample of an example 10 -- the parent phase in a CoNiCrAlY layer -- an interface with a diffusion barrier layer to 14 micrometers ***** -- although it had disappeared -- the other part -- remaining -- scaling object layer thickness 5 micrometers It was controlled by extent. It is in ** to have the effectiveness that the diffusion barrier layer of this invention carries out long duration continuation of the oxidation resistance, from the above result.

[0076] A nickel-14%aluminum alloy (% of the weight) is used for the front face of the base material which consists of example 11 nickel radical superalloy IN-738LC as a thermal-spraying raw material on the front face, and it is 20 micrometers in thickness with a low-pressure-plasma-spraying method. The diffusion barrier layer was formed. Subsequently, it is thickness about a NiCoCrAlY layer (the same presentation as an example 8). 120 micrometers Covering formation was carried out. Moreover, the sample of the same configuration was produced as an example of a comparison with this invention except not forming a diffusion barrier layer. In then, these samples 1393Kx2h+1123Kx24h It heat-treated.

[0077] SEM observation of the cross section of each sample was performed after heat treatment, and the phase configuration like each part was investigated. Consequently, as for a base material, an example and the example of a comparison consist of a gamma+gamma' phase, and an example the rate of the volume of gamma' phase The example of a comparison 42% It was 44%. Moreover, as for a NiCoCrAlY layer, which sample consists of gamma+ parent phases, and an example the rate of the volume of a parent phase The example of a comparison 51% It was 49%. The diffusion barrier layer in an example makes gamma phase a matrix, and is a rate of the volume. It had become the configuration that 73% of gamma' phase deposited.

[0078] Each sample by these examples and the example of a comparison The oxidation test in atmospheric air of 1173Kx 5000h was presented. the result of having done SEmu observation of the cross section of each sample after the trial -- example of a comparison the parent phase in a NiCoCrAlY layer -- from a base material interface 100 micrometers up to -- perfect -- disappearing - - moreover, rate of the volume of the remainder It had become 11% or less. The oxidation resistance

of this enveloping layer falls remarkably by disappearance of aluminum, and is 12 micrometers from a front face. The scaling film was growing to thickness. on the other hand -- the sample by the example -- a diffusion barrier layer to 14 micrometers although the parent phase had disappeared to thickness -- the remainder -- parent phase 46% or more -- existing -- carrying out -- **** -- such anti-oxidation effectiveness -- a surface oxide layer -- 3 micrometers up to -- **** -- it was not growing up. The above result showed that the diffusion prevention layer of this invention had effectiveness in oxidation-resistant long duration maintenance.

[0079] example 12Co radical superalloy FSX-414 from -- the front face of the becoming base material -- a Co-17%Cr-24%aluminum alloy (% of the weight) -- as a thermal-spraying raw material -- using -- a low-pressure-plasma-spraying method -- 23 micrometers in thickness The diffusion barrier layer was formed. Subsequently, it is thickness about a CoNiCrAlY layer (the same presentation as an example 10). 130 micrometers Covering formation was carried out. Moreover, the sample of the same configuration was produced as an example of a comparison with this invention except not forming a diffusion barrier layer. In then, these samples 1423Kx4h+1198K x10h+813Kx 24h was heat-treated. The result of having gazed at the cross-section organization of each [these] sample by SEMu, and having investigated the configuration of each class, as for a CoNiCrAlY layer, an example and the example of a comparison consist of a gamma phase (Co solid solution) matrix and a parent phase (CoAl phase), and the rate of the volume of a parent phase is at an example. In 47% and the example of a comparison It was 43%. Moreover, a diffusion barrier layer also consists of a gamma phase and a parent phase, and it is the rate of the volume of a parent phase. It was 72%. [0080] each of these samples 1173Kx5000h the result with which the oxidation test in quiescence atmospheric air was presented -- sample of the example of a comparison the parent phase in a CoNiCrAlY layer -- perfect -- disappearing -- a surface oxide layer -- 25 micrometers up to -- it was growing up. - sample of a way and an example the parent phase of a CoNiCrAlY layer -- a diffusion barrier layer interface to 17 micrometers up to -- although it had disappeared -- the remainder 38% or more -- existing -- **** -- moreover, surface oxide layer 7 micrometers up to -- **** -- it was not growing up.

[0081] A nickel-13%aluminum alloy (% of the weight) is used for the front face of the base material which consists of example 13 single-crystal nickel radical superalloy CMSX-2 as a thermal-spraying raw material, and it is 23 micrometers in thickness with a low-pressure-plasma-spraying method. The diffusion barrier layer was formed. It ranks second. It is thickness about a NiCoCrAlY layer (the same presentation as an example 8). 120 micrometers Covering formation was carried out. On furthermore, this front face ZrO₂-8wt%Y₂O₃ It is thickness with an atmospheric-air plasma metal spray method about a layer. 230-micrometer covering formation was carried out. moreover, as an example of a comparison with this invention, the sample (however, a NiCoCrAlY layer -- thickness [] -- thickness [] (130 micrometers and ZrO₂-8wt%Y₂O₃ layer) -- it could be 240 micrometers) of the same configuration was produced except not forming a diffusion barrier layer. The result of SEMu observation of the cross section of each [these] sample, a NiCoCrAlY layer consists of a gamma phase (nickel solid solution) and a parent phase (NiAl phase), and the rate of the volume of a parent phase is at an example. In 53% and the example of a comparison It was 50%. Moreover, a base material consists of a gamma phase and a gamma' phase (nickel3aluminum phase), and the rate of the volume of gamma' phase is at an example. In 61% and the example of a comparison It was 59%. It consists of a gamma phase and a gamma' phase, and a diffusion barrier layer is the rate of the volume of gamma' phase. It was 87%. Each [these] sample 1173Kx5000h The oxidation test in quiescence atmospheric air was presented. the result of having performed SEM observation of a cross section after the trial -- example of a comparison the parent phase in a NiCoCrAlY layer -- a base material interface to 90 micrometers up to -- it disappears completely -- ZrO₂ An interface with a layer to 14 micrometers The oxide layer formed to thickness. on the other hand -- the sample of an example -- the parent phase in a NiCoCrAlY layer -- a diffusion prevention layer interface to 17 micrometers up to -- **** -- not disappearing -- the remainder -- 19% The parent phase remained at the above rate of the volume. moreover -- ZrO₂ Also oxide layer thickness by the side of an interface with a layer 3 micrometers With extent, oxidation resistance was markedly alike and is improved. [0082] A nickel-17%Ti-5%aluminum alloy (% of the weight) is used for the front face of the base material which consists of example 14 single-crystal nickel radical superalloy CMSX-2 as a thermal-

spraying raw material, and it is 25 micrometers in thickness with a low-pressure-plasma-spraying method. The diffusion barrier layer was formed. Subsequently, it is thickness about a NiCoCrAlY layer (the same presentation as an example 8). 130 micrometers Covering formation was carried out. On furthermore, the front face ZrO₂-8wt%Y₂O₃ It is 210 micrometers in thickness with an atmospheric-air plasma metal spray method about a layer. Covering formation was carried out. Moreover, the sample of the same configuration was produced as an example of a comparison with this invention except not forming a diffusion barrier layer. In each [these] sample 1323Kx16h+1123Kx48h After heat-treating, as a result of performing SEMu observation of a cross section, a base material consists of a gamma phase (nickel solid solution) and a gamma' phase (nickel3 aluminum), and the rate of the volume of gamma' phase is at an example. In 55% and the example of a comparison It was 54%. Moreover, a NiCoCrAlY layer consists of a gamma phase and a parent phase, and the rate of the volume of a parent phase is at an example. In 43% and the example of a comparison It was 46%. Furthermore, a diffusion barrier layer consists of a gamma phase and an eta phase (nickel3 Ti phase), and is the rate of the volume of eta phase. It was 74%. [0083] Each of these samples 1173Kx5000h The oxidation test in quiescence atmospheric air was presented. As a result of performing SEM observation of a cross section after a trial, it is at the sample of the example of a comparison. The parent phase in a NiCoCrAlY layer disappears completely. ZrO₂ an interface with a layer -- 19 micrometers the oxide layer formed -- receiving -- sample of an example the parent phase in a NiCoCrAlY layer -- a diffusion barrier layer interface to 13 micrometers *****, although it had disappeared By the other part It remains 12% or more and is a pan. ZrO₂ Also oxide layer thickness by the side of an interface with a layer 4 micrometers It was extent. This invention became clear [having effectiveness in oxidation-resistant maintenance] from the above result.

[0084]

[Effect of the Invention] since exfoliation between each class etc. can be prevented while according to the heat-resistant member of this invention carrying out long duration maintenance of anticorrosion and the oxidation resistance and being able to control the fall of the high temperature strength of a base material, as explained above, it becomes possible to boil the dependability and the life of a heat-resistant member markedly, and to raise them. It follows, for example, even if it is under thermal stress, oxidation, and the environment where corrosion is overlapped further and it acts, like a gas turbine aerofoil, the heat-resistant member which can maintain anticorrosion, the outstanding oxidation resistance, and outstanding high temperature strength over a long time can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing 1 operation gestalt of the 1st heat-resistant member of this invention.

[Drawing 2] It is the sectional view showing the condition or real busy condition of a heat treatment word of the heat-resistant member shown in drawing 1.

[Drawing 3] It is the sectional view showing the condition of having carried out covering formation of the ceramic layer in the heat-resistant member shown in drawing 1.

[Drawing 4] It is the sectional view showing 1 operation gestalt of the 2nd heat-resistant member of this invention.

[Drawing 5] It is the sectional view showing the condition of having carried out covering formation of the ceramic layer in the heat-resistant member shown in drawing 4.

[Description of Notations]

- 1 11 Metal base
- 2 Metal layer which dissolves oxygen and nitrogen
- 3 13 M-Cr-aluminum-Y alloy layer
- 4, 7, 14, 16 Heat-resistant member
- 5 An oxide or nitrides, such as aluminum
- 12 Diffusion barrier layer
- 15 Ceramic layer

[Translation done.]

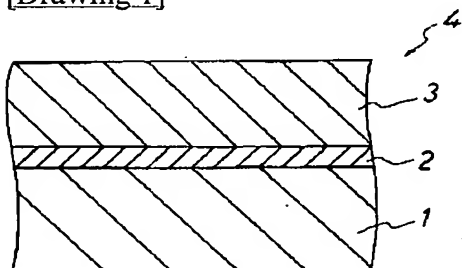
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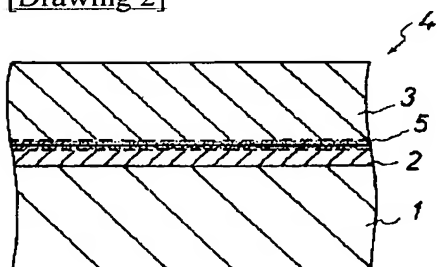
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DRAWINGS

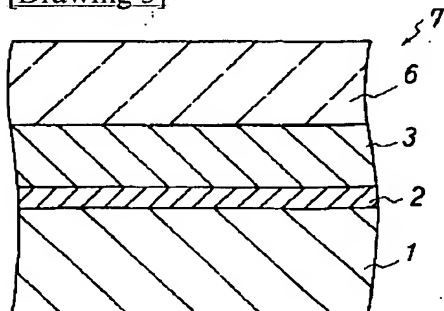
[Drawing 1]



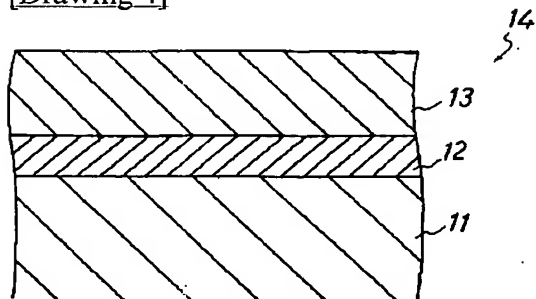
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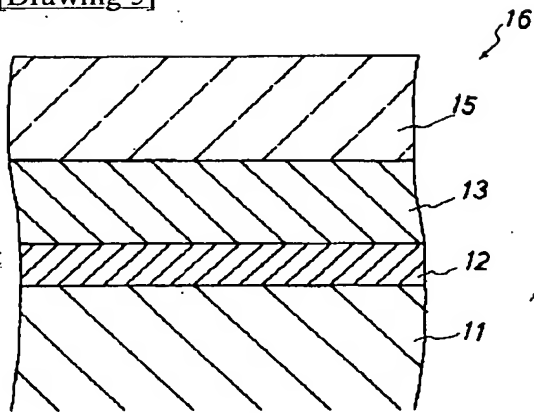
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]